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Manual for Implementing Residual Radioactive Material Guidelines Using RESRAD, Version 5.0

Working Draft for Comment

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CONTENTS

CONTENTS (Cont)

CONTENTS (Cont.)

APPENDIX E

WATER PATHWAY FACTORS

Water pathway factors are components of the environmental transport factors for water-dependent ingestion pathways. A water-dependent ingestion pathway can be divided into two segments (1) a water pathway segment that extends from the contaminated zone to a point where transport through the food chain begins (a well or surface water body) and (2) a food chain pathway segment that extends from the point of entry of a radionuclide from water into the food chain to a point of human exposure. Transport through the water pathway segment is characterized by a water/soil concentration ratio, which is defined as the ratio of the concentration of the principal radionuclide (either parent or progeny) in water used for drinking, irrigation, or livestock water to the initial parent radionuclide concentration in the contaminated zone. Transport through the food chain pathway segment is characterized by a water exposure factor, which is defined as the ratio of the quantity of a radionuclide ingested annually to the concentration in water used for drinking, irrigation, or livestock water. The environmental transport factor for the water-dependent ingestion pathway can be expressed as a product of a water exposure factor and a water/soil concentration ratio

$$ETF_{ij,pqr}(t) = WEF_{ij,pqr}(t) \times WSR_{ij,r}(t) , \qquad \text{(E 1)}$$

where

$ETF_{ij,pqr}(t)$ = $E_{ij,pqr}(t)/S_i(0)$ = environmental transport factor at time t for the jth principal radionuclide transported through the pqrth ingestion pathway (g/yr) — $E_{ij,pqr}(t)$ is the rate of ingestion (pCi/yr) at time t of the jth principal radionuclide transported through the pqrth pathway from the contaminated zone to a point of human exposure, and $S_i(0)$ is the initial concentration (pCi/g) of the ith principal radionuclide in the contaminated zone,

ij = subscript index of a variable whose quantity is assigned to the principal radionuclide j as the result of the decay of the

principal radionuclide i, which initially exists in the contaminated zone [1]

p, q, r = pathway indices — the indices p and q identify the food chain segment of the pathway (see Table 2 1 and Equation D 1), and the index r identifies the water pathway segment, that is, the segment from the contaminated zone to well water ($r = 1$) or surface water ($r = 2$),

$WEF_{ij,pqr}(t)$ = $E_{ij,pqr}(t)/W_{ij,r}(t)$ = water exposure factor at time t for the jth principal radionuclide transported through the pqrth pathway from the point of water use to the point of exposure (L/yr) — $E_{ij,pqr}(t)$ is the rate of ingestion (pCi/yr) at time t of the jth principal radionuclide transported through the pqrth pathway, and $W_{ij,r}(t)$ is the concentration in water (pCi/L) at time t of the jth principal radionuclide transported through the rth water pathway segment at the point of entry into the pqth food chain, and

$WSR_{ij,r}(t)$ = $W_{ij,r}(t)/S_i(0)$ = water/soil concentration ratio at time t for the rth water pathway segment (g/L) — $W_{ij,r}(t)$ is the concentration in water (pCi/L) at time t of the jth principal radionuclide transported through the rth water pathway segment at the point of entry into a food chain pathway segment, and $S_i(0)$ is the average concentration (pCi/g) at time 0 of the ith principal radionuclide in the contaminated zone

The water exposure factor $WEF_{ij,pqr}(t)$ is discussed in Appendix D   The water/soil concentration ratio $WSR_{ij,r}(t)$ is discussed in this appendix and Appendix I

A water soil concentration ratio, $WSR_{ij,r}$ is determined by the rate at which the parent radionuclide i is leached from the contaminated zone, the amount of ingrowth of radionuclide j from radionuclide i along the water pathway from the boundary of the

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[1] In the remainder of this appendix, a variable with a subscript index of ij refers directly to radionuclide j However, the quantity of the variable is actually associated with the ingrowth and decay relationship between radionuclides j and i

contaminated zone to the point of water use, the time for radionuclide j and its precursors of the same decay chain to be transported along the water pathway, and the dilution that occurs along this pathway The model for estimating radionuclide leaching and formulas for calculating the leach rate are given in Section E 1 Formulas that relate the radionuclide concentration in water at the point of use to parameters that characterize the leaching and transport processes are derived in Section E 2 Formulas of dilution factors and other transport parameters used to calculate $WSR_{ij,r}$ are given in Section E 3 The transfer functions of radioactive decay products transporting through the unsaturated zone and saturated zone are discussed in Appendix I

E.1 RADIONUCLIDE LEACHING FROM THE CONTAMINATED ZONE

Radionuclides adsorbed in soil are subject to leaching by infiltrating water Radionuclides leaching from the contaminated zone are the sources of groundwater contamination Therefore, the first step in calculating radionuclide concentrations in groundwater is to estimate the leaching of radionuclides from the contaminated zone

A sorption-desorption, ion-exchange leaching model is used in the RESRAD code This model is characterized by a nuclide-dependent, first-order leach rate constant, L_i, which is defined as the fraction of available radionuclide i leached out per unit time The radionuclide release rate (source strength, in pCi/yr), $R_i(t)$, can be written as (Yu 1987)

$$R_i(t) = L_i \ \rho_b^{(cz)} \ A \ T(t) \ S_i(t) \ , \tag{E 2}$$

where

L_i = leach rate for radionuclide i (yr^{-1}),

$\rho_b^{(cz)}$ = bulk density of the contaminated zone (kg/m^3),

A = area of the contaminated zone (m^2),

$T(t)$ = thickness of the contaminated zone at time t (m), and

$S_i(t)$ = average concentration of the ith principal radionuclide in the contaminated zone available for leaching at time t (pCi/kg)

The first-order leach rate constant used in the current version of RESRAD is a time-independent radionuclide leach rate constant that is estimated on the basis of the soil

residence time for the initial thickness of the contaminated zone   A time-independent radionuclide leach rate constant for radionuclide i, L_i, may be written as

$$L_i = \frac{I}{\theta^{(cz)} \, T_0 \, R_{d_i}^{(cz)}} \, ,$$

(E 3)

where

I = infiltration rate (m/yr),

$\theta^{(cz)}$ = volumetric water content of the contaminated zone, and

T_0 = initial thickness of the contaminated zone (m), and

$R_{d_i}^{(cz)}$ = retardation factor in the contaminated zone for radionuclide i (dimensionless).

The infiltration rate is given by

$$I = (1 - C_e)[(1 - C_r)P_r + I_{rr}] \, ,$$

(E 4)

where

C_e = evapotranspiration coefficient (0 5, dimensionless),

C_r = runoff coefficient (0 2, dimensionless),

P_r = precipitation rate (annual rainfall, 1 0 m/yr), and

I_{rr} = irrigation rate (0 2 m/yr)

To calculate the infiltration rate, the average evapotranspiration coefficient is used rather than the average evapotranspiration rate, E_t (see Geraghty et al [1973] for U S average) Using the average evapotranspiration rate does not take into account the correlation between precipitation and evapotranspiration and, for arid regions, can give a spurious negative infiltration rate   The evapotranspiration coefficient is related to the evapotranspiration rate by the formula $C_e = E_t/[(1 - C_r)P_r + I_{rr}]$ Runoff coefficients for a specific site may be obtained from Table E 1 It is assumed that irrigation water is controlled by ditching or by the duration of application so that none will be lost by runoff The default irrigation rate is for humid regions where irrigation is unnecessary, an appropriate generic

TABLE E.1 Runoff Coefficient Values

Type of Area	Coefficient	Value
Agricultural environment[a]		
Flat land with average slopes of 0 3 to 0 9 m/mi	c_1	0 3
Rolling land with average slopes of 4 6 to 6 1 m/mi	c_1	0 2
Hilly land with average slopes of 46 to 76 m/mi	c_1	0 1
Open sandy loam	c_2	0 4
Intermediate combinations of clay and loam	c_2	0 2
Tight, impervious clay	c_2	0 1
Woodlands	c_3	0 2
Cultivated lands	c_3	0 1
Urban environment		
Flat, residential area — about 30% impervious	C_r	0 4
Moderately steep, residential area — about 50% impervious	C_r	0 65
Moderately steep, built-up area — about 70% impervious	C_r	0 8

[a] The runoff coefficient for an agricultural environment is given by $C_r = 1 - c_1 - c_2 - c_3$

Source Data from Gray (1970)

value for arid regions would be $I_{rr} = 1$ m/yr Site-specific values for the precipitation and irrigation rates should be used whenever possible

The volumetric water content of the contaminated zone, $\theta^{(cz)}$, is the product of the saturated water content of the contaminated zone, $\theta_{sat}^{(cz)}$, and the saturation ratio of the contaminated zone, $R_s^{(cz)}$ The saturated water content is the water content when the soil material is saturated Hence, θ_{sat} equals p_t, where p_t is the total porosity of the soil material, that is,[2]

$$\theta_{sat} = p_t \qquad (E\ 5)$$

The saturation ratio, R_s, is defined as the ratio of θ over θ_{sat}, that is,

[2] The superscript is omitted for a general definition The definition applies for all zones

$$R_s = \theta/\theta_{sat} = \theta/p_t \qquad \text{(E 6)}$$

When the medium is saturated, R_s equals unity Under unsaturated infiltration conditions, the saturation ratio is a function of the infiltration rate, the saturated hydraulic conductivity, and the texture of the soil The saturation ratio can be estimated by using the following equation (Clapp and Hornberger 1978)

$$R_s = \left(\frac{I}{K_{sat}}\right)^{\frac{1}{2b + 3}}, \qquad \text{(E 7)}$$

where

I = infiltration rate (m/yr),

K_{sat} = saturated hydraulic conductivity (m/yr), and

b = soil-specific exponential parameter (dimensionless)

Representative values of K_{sat}, θ_{sat}, and b for various soil textures are listed in Table E 2

TABLE E.2 Representative Values of Saturated Hydraulic Conductivity, Saturated Water Content, and the Soil-Specific Exponential Parameter

Texture	Hydraulic Conductivity, K_{sat} (m/yr)	Saturated Water Content, θ_{sat}	Soil-Specific Exponential Parameter, b
Sand	$5\ 55 \times 10^3$	0 395	4 05
Loamy sand	$4\ 93 \times 10^3$	0 410	4 38
Sandy loam	$1\ 09 \times 10^3$	0 435	4 90
Silty loam	$2\ 27 \times 10^2$	0 485	5 30
Loam	$2\ 19 \times 10^2$	0 451	5 39
Sandy clay loam	$1\ 99 \times 10^2$	0 420	7 12
Silty clay loam	$5\ 36 \times 10^1$	0 477	7 75
Clay loam	$7\ 73 \times 10^1$	0 476	8 52
Sandy clay	$6\ 84 \times 10^1$	0 426	10 40
Silty clay	$3\ 26 \times 10^1$	0 492	10 40
Clay	$4\ 05 \times 10^1$	0 482	11 40

Source Data from Clapp and Hornberger (1978)

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The retardation factor for radionuclide ι, R_{d_ι}, is the ratio of the average pore water velocity to the radionuclide transport velocity Assuming that the adsorption-desorption process can be represented with a linear Freundlich isotherm, the retardation factor can be calculated with the following formula (Yu 1987)

$$R_{d_\iota} = 1 + \frac{\rho_b K_{d_\iota}}{\theta} = 1 + \frac{\rho_b K_{d_\iota}}{p_\iota R_s} , \qquad \text{(E 8)}$$

where

ρ_b = bulk soil density (g/cm^3),

K_{d_ι} = distribution coefficient for the ιth principal radionuclide (cm^3/g), and

θ = volumetric water content (dimensionless)

The distribution coefficient is the radionuclide equilibrium concentration ratio of the adsorbed radionuclide (in soil) to the desorbed radionuclide (in water). Representative distribution coefficients are given in Tables E 3 through E 6

E.2 WATER/SOIL CONCENTRATION RATIOS IN TERMS OF NUCLIDE WATER-TRANSPORT PARAMETERS

A water/soil concentration ratio can be expressed in terms of functions that characterize the source terms and transport processes and that are applicable for both simple and complex hydrogeological strata By introducing simplifying approximations for the functional form of the breakthrough curve that are generally applicable, even for complex hydrogeological structures, the transport and source functions can be specified by a small number of nuclide water-transport parameters Various models can be used to derive the relationships between these parameters and measurable quantities The analysis is applicable to either the groundwater or surface water pathway, hence, in the following derivation, the subscript r that is used to identify different water pathways has been omitted in order to simplify the expressions

According to the definitions presented in Equation E 1, the water/soil concentration ratio, $WSR_{\iota j}(t)$, can be expressed as

$$WSR_{\iota j}(t) = \frac{W_{\iota j}(t)}{S_\iota(0)} , \qquad \text{(E 9)}$$

TABLE E.3 Typical Average Distribution Coefficients for Various Elements in Sand, Soils, and Clays

Element	Average Distribution Coefficient,[a] K_d (cm³/g)		Geometric Standard Deviation	Element	Average Distribution Coefficient,[a] K_d (cm³/g)		Geometric Standard Deviation
	Soils and Clays	Sand[b]			Soils and Clays	Sand	
As	3	0 3	1 8	Hg	100	10	-
Ba	50	5	-	Ni	1,000	100	-
Cd	7	0 7	2 4	Pu	2,000	200	10
Ce	1,000	100	3 7	Ra[d]	70	7	7
Cs[c]	500	80	2 4	Se	3	0 3	1 9
Cr (+6)	4	0 4	9 0	Ag	100	10	3 7
Co	1,000	100	-	Sr[d,e]	30	3	7 4
Cu	20	2	3 0	Th	60,000	6,000	4 5
F	0	0	-	Tritium	0	0	-
Fe	1,000	100	-	U	50	5	3 6
La	1,000	100	-	Va	1,000	100	-
Pb	100	10	5 5	Zn	20	2	6 7
Li	500	50	-	Zr	1,000	100	-
Mn	200	20	15				

[a] Data for As, Cd, Ce, Cr, Co, Cu, Pb, Mn, Pu, Se, Ag, Sr, Th, U, and Zn from Baes and Sharp (1983), the values of K_d are the geometric means of the literature data (see also Gilbert et al 1983, pp 3-57 to 3-60). Data for other elements from Nuclear Safety Associates (1980), except as noted All values have been rounded to one significant figure

[b] The values are taken to be 10% of the values of soils and clays (Nuclear Safety Associates 1980), except for Cs

[c] From Isherwood (1981), using soil and quartz sand data, rounded to one significant digit

[d] Sources U S Nuclear Regulatory Commission (1980), Gee et al (1980)

[e] The corresponding values from Isherwood (1981) for Sr are 73 for soils, 2 5 for quartz sand, and 24 for other sands

TABLE E.4 Distribution Coefficients for Strontium and Cesium[a]

Conditions	K_d (cm³/g)	
	Strontium	Cesium
Basalt, 32-80 mesh	16-140	790-9,500
Basalt, 0 5-4 mm, 300 ppm TDS	220-1,200	39-280
Basalt, 0 5-4 mm, sea water	1 1	6 5
Basalt-fractured in-situ measurement	3	
Sand, quartz - pH 7 7	1 7-3 8	22-310
Sands	13-43	100
Carbonate, greater than 4 mm	0 19	14
Dolomite, 4,000 ppm TDS	5-14	
Granite, greater than 4 mm	1 7	34
Granodiorite, 100-200 mesh	4-9	8-9
Granodiorite, 0 5-1 mm	11-23	1,000-1,800
Hanford sediments	50	300
Tuff	45-4,000	800-18,000
Soils	19-280	190-1,100
Shaley siltstone, greater than 4 mm	8	310
Sandstone, greater than 4 mm	1 4	100
Alluvium, 0 5-4 mm	48-2,500	120-3,200
Salt, greater than 4 mm, saturated brine	0 19	0 027

[a] All values have been rounded to two significant figures

Source Data from Isherwood (1981)

where $WSR_{ij}(t)$ is given in units of (g/L), and $W_{ij}(t)$ is the average concentration at time t of the jth principal radionuclide in water at the point of use in units of pCi/L due to the original concentration at $t = 0$ of the ith principal radionuclide, $S_i(0)$, in units of pCi/g

The concentration of the jth principal radionuclide at the point of use at time t as a result of the original contamination of the ith principal radionuclide, $W_{ij}(t)$, is the sum of all contributions from the decay products of the original contamination, $S_i(0)$, which was leached from the contaminated zone at a time earlier than t If k is a radionuclide in the decay chain from i to j (i and j inclusive), the concentration of radionuclide k in the contaminated zone resulting from an original contamination of the ith radionuclide $S_i(0)$ can be expressed as follows by using the source factor SF_{ik} as defined in Section 3 2 3 and Appendix G

$$S_k(t) = S_i (0) SF_{ik}(t)$$

(E 10)

13

TABLE E.5 Distribution Coefficients for Thorium and Uranium

Conditions	K_d (cm^3/g)
Thorium	
Silt loam, Ca-saturated clay, pH 6 5	160,000
Montmorillonite, Ca-saturated clay, pH 6 5	400,000
Clay soil, 5 mM Ca(NO$_3$)$_2$, pH 6 5	160,000
Medium sand, pH 8 15	40-130
Very fine sand, pH 8 15	310-470
Silt/clay, pH 8 15	270-10,000
Schist soil, 1 g/L Th, pH 3 2	8
Schist soil, 0 1 g/L Th	603 2
Illite, 1 g/L Th, pH 3 2	120
Illite, 0 1 g/L Th, pH 3 2	1,000
Illite, 0 1 g/L Th, pH > 6	<100,000
Uranium	
Silt loam, U(VI), Ca-saturated, pH 6 5	62,000
Clay soil, U(VI), 5 mM Ca(NO$_3$)$_2$, pH 6 5	4,400
Clay soil, 1 ppm UO^{+2}, pH 5 5	300
Clay soil, 1 ppm UO^{+2}, pH 10	2,000
Clay soil, 1 ppm UO^{+2}, pH 12	270
Dolomite, 100-325 mesh, brine, pH 6 9	4 5
Limestone, 100-170 mesh, brine, pH 6 9	2 9

Source Data from Isherwood (1981)

The release rate (atoms/yr) of k atoms from the contaminated zone into the unsaturated zone can be written by substituting the following in Equation E 2

$$\dot{R}_{ik}(t) = \frac{SF_{ik}(t)\ S_i(0)}{\lambda_k}\ L_k \rho_b^{(cz)}\ T(t)\ A \times constant\ ,$$ (E 11)

where λ_k is the decay constant of radionuclide k and *constant* is a unit conversion factor Use of the leach rate as defined in Equation E 3 yields

$$\dot{R}_{ik}(t) = \frac{SF_{ik}(t)\ S_i(0)}{\lambda_k}\ \frac{I}{\theta^{cz}\ T_0\ R_{d_k}^{(cz)}}\ \rho_b^{(cz)}\ T(t)\ A \times constant$$ (E 12)

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TABLE E 6 Distribution Coefficients for Several Radionuclides from Various Sources

Element	pH	K_d (cm³/g)	Source	Element	pH	K_d (cm³/g)	Source
Uranium	2	0	Rancon (1973)	Lead	2 2	1,850	Gee et al (1980)
	8	100			7 7	10,000	
	10	600					
	13	50			4-9	99[c]	Baes and Sharp (1983)
	2 2	1 3	Gee et al (1980)	Strontium	2	0 1	Staley et al (1979)
	7 7	23,000			3	6	
					7	500	
	4-9	45[a]	Baes and Sharp (1983)		10	170	
Thorium	2	500	Rancon (1973)		4-9	27[d]	Baes and Sharp (1983)
	5	3,000					
	7	50,000		Cesium	3	45	Staley et al (1979)
	13	50			5	150	
					8	905	
	2.2	1.2	Gee et al (1980)		10	650	
	7 7	80,000					
					4-9	1,100[e]	Baes and Sharp (1983)
	4-9	60,000[b]	Baes and Sharp (1983)				
Radium	2	0	U S Nuclear	Plutonium	2	150	Staley et al (1979)
	4	12	Regulatory		5	250	
	6	60	Commission (1980)		7	8,500	
	7	100			11	1,000	
					4-9	1,800[f]	Baes and Sharp (1983)
	2 2	13	Gee et al (1980)				
	7 7	2,400		Deuterium	All	0	

[a] Geometric mean (GM) of values ranging from 11 to 4,400, with a geometric standard deviation (GSD) of 3 7

[b] GM of values ranging from 2,000 to 510,000, with a GSD of 4 5

[c] GM of values ranging from 4 5 to 7,600, with a GSD of 5 5

[d] GM of values ranging from 0 15 to 3,300, with a GSD of 7 4

[e] GM of values ranging from 10 to 52,000, with a GSD of 6 7

[f] GM of values ranging from 11 to 300,000, with a GSD of 10

The transfer function, $G_{kj}(t)$ is defined as follows if N_k atoms of radionuclide k are released at time t_0 from the contaminated zone into the unsaturated zone, $n_j(t)\, dt = N_k\, G_{kj}\, (t\text{-}t_0)\, dt$ atoms of radionuclide j will arrive at the point of use between t and $t + dt$ This function is developed in Appendix I

The release rate, $R_{ik}(t)$ of k atoms into the unsaturated zone will result in a release of j atoms from the saturated zone to the point of use of

$$r_{kj}(t) = R_{ik}(t) \bullet G_{kj}(t) = \int_0^t R_{ik}(t') \, G_{kj}(t-t') \, dt \quad , \tag{E 13}$$

where the asterisk is used to denote the time convolution of the functions, and $r_{kj}(t)$ is the release amount of radionuclide j at the point of use at time t due to the release of radionuclide k from the contaminated zone

The concentration of j at the point of use resulting from k atoms being released from the contaminated zone can be estimated by dividing the activity by the water flow rate, IA, and multiplying by the dilution factor, f

$$W_{kj}(t) = \frac{\lambda_j \, r_{kj}(t) \, f}{I \, A \times constant} \tag{E 14}$$

The water/soil concentration, WSR_{ij}, can be derived by summing the concentrations of nuclide j from all the decay products of nuclide i, that is, nuclide k (which then will decay to nuclide j) and then dividing by the original contamination of i, $S_i(0)$

$$WSR_{ij}(t) = \frac{\sum_k \dfrac{\lambda_j \, r_{kj}(t) \, f}{IA \; constant}}{S_i(0)} \tag{E 15}$$

$$= \frac{\lambda_j \rho_b^{cz} \, f}{\theta^{cz} T_0} \sum_k \left(\frac{SF_{ik}(t) \, T(t)}{\lambda_k R_{d_k}^{(cz)}} \right) \bullet G_{kj}(t) \tag{E 16}$$

By defining the source-term leaching ratio, $Q_j(t)$, as

$$Q_j(t) = \frac{T(t)}{T_0 \, R_{d_j}^{(cz)}} \quad , \tag{E 17}$$

$WSR_{ij}(t)$ can be explicitly written as

$$WSR_{ij}(t) = \frac{\lambda_j \rho_b^{cz} f}{\theta^{cz}} \sum_k \int_0^t \frac{SF_{ik}(t') Q_k(t')}{\lambda_k} G_{kj}(t-t') \, dt \tag{E 18}$$

16

E.3 WATER TRANSPORT PARAMETERS

E.3.1 On-Site Groundwater Pathway ($r = 1$)

The water transport parameters for radionuclide i are the breakthrough time Δt_i (the time following the radiological survey at which radionuclides first appear in the water at the point of use), the rise time δt_{ir} (the time following the breakthrough time for the radionuclide concentration in the water to attain a maximum value), and the dilution factor f_{ir} (the ratio between the concentration in the water at the point of use to the concentration in the infiltrating water as it leaves the unsaturated zone). Two models are used for calculating these parameters a mass-balance (MB) model and a nondispersion (ND) model. In the MB model, it is assumed that all of the radionuclides released from the contaminated zone are withdrawn through the well. In the ND model, it is assumed that the dispersivity is nil, the unsaturated zone consists of one or more horizontal homogeneous strata, the saturated zone is a single homogeneous stratum, and water withdrawal introduces only a minor perturbation in the water flow. These assumptions lead to a pattern of flow lines from which the dilution factor can be estimated by geometric considerations.

The user has the option of selecting which model to use. Usually, the MB model is used for smaller contaminated areas (e g , 1,000 m^2 or less) and the ND model is used for larger areas. The breakthrough times are the same for both models, the rise times and dilution factors are different.

E.3.1.1 Breakthrough Time

The well from which water is withdrawn for domestic use or irrigation is conservatively assumed to be located either in the center of the contaminated zone (in the MB model) or at the downgradient edge of the contaminated zone (in the ND model). For either location, radionuclides are assumed to enter the well as soon as they reach the water table, hence, the transport time through the aquifer is nil and the breakthrough time is equal to the transport time through the unsaturated zone, which is the sum of the times that a radionuclide is transported through those strata of the unsaturated zone that lie below the contaminated zone

$$\Delta t_i = \sum_{m=1}^{n+1} \Delta t^{(uz)}_{im} , \qquad \text{(E 19)}$$

where

n = number of distinct horizontal strata in the unsaturated zone below the contaminated zone at time 0, and

$\Delta t^{(uz)}_{im}$ = transport time for the ith principal radionuclide through the mth stratum (yr)

The upper bound, $n+1$, of the summation in Equation E 19 is for the $(n+1)$th unsaturated stratum created by the decrease in the water table The thickness of this $(n+1)$th stratum, Δz_{n+1}, is equal to the product of the water table drop rate, v_{wt}, and time That is,

$$\Delta z_{n+1} = v_{wt} \times t , \qquad \text{(E 20)}$$

where v_{wt} = water table drop rate (0 001 m/yr)

The hydrogeological and hydrogeochemical properties of the $(n+1)$th unsaturated stratum are assumed to be the same as those of the saturated stratum The RESRAD code allows up to five horizontal strata below the contaminated zone, that is, $n \leq 5$ If $n = 0$, the contaminated zone extends down to the aquifer

The formula for the transport time is

$$\Delta t^{(uz)}_{im} = \frac{\Delta z_m \, R^{(uz)}_{d_{im}} \, p^{(uz)}_{e_m} \, R^{(uz)}_{s_m}}{I} , \qquad \text{(E 21)}$$

where

Δz_m = thickness of the mth stratum ($\Delta z_1 = 4$ m, Δz_2, , $\Delta z_5 = 0$),

$R^{(uz)}_{d_{im}}$ = retardation factor of the ith principal radionuclide in the mth stratum of the unsaturated zone,

$P_{e_m}^{(uz)}$ = effective porosity of the mth stratum of the unsaturated zone (0 2, dimensionless), and

$R_{s_m}^{(uz)}$ = saturation ratio of the mth stratum (dimensionless)

The unsaturated zone retardation factors, $R_{d_{im}}^{(uz)}$, are calculated by the formula

$$R_{d_{im}}^{(uz)} = 1 + \frac{\rho_{b_m}^{(uz)} K_{d_{im}}^{(uz)}}{\left(p_{t_m}^{(uz)} R_{s_m}^{(uz)} \right)} , \qquad (E\ 22)$$

where

$\rho_{b_m}^{(uz)}$ = bulk soil density in the mth stratum (1 5 g/cm^3),

$K_{d_{im}}^{(uz)}$ = distribution coefficient for the ith principal radionuclide in the mth stratum (cm^3/g), and

$p_{t_m}^{(uz)}$ = total porosity of the mth stratum (0 4, dimensionless)

The saturation ratio, $R_{s_m}^{(uz)}$, can be determined by using Equation E 7

Data that may be used to estimate breakthrough times when site-specific measurements are not available are given in Tables E 2 through E 7, as follows saturated water contents (porosities), soil-specific exponential parameters, and saturated hydraulic conductivities are given in Table E 2, distribution coefficients are given in Tables E 3 through E 6, and total porosities and effective porosities are given in Table E 7

Hydraulic conductivity is a critical hydrological parameter that can differ by several orders of magnitude from one site to another Site-specific values should be used for deriving soil guidelines Default values of the distribution coefficient values used in the RESRAD code are the values for soils and clays given in Table E 3 The default distribution coefficient for technetium is zero For other elements not listed in Table E 3, the default value is the value of the nearest listed element in the same column of the periodic table If there are no other elements in the same column, a zero value is assumed

TABLE E.7 Representative Porosity Values

Material	Total Porosity, p_t		Effective Porosity, p_e	
	Range	Arithmetic Mean	Range	Arithmetic Mean
Sedimentary material				
Sandstone (fine)	-	-	0 02-0 40	0 21
Sandstone (medium)	0 14-0 49	0 34	0 12-0 41	0 27
Siltstone	0 21-0 41	0 35	0 01-0 33	0 12
Sand (fine)	0 25-0 53	0 43	0 01-0 46	0 33
Sand (medium)	-	-	0 16-0 46	0 32
Sand (coarse)	0 31-0 46	0 39	0 18-0 43	0 30
Gravel (fine)	0 25-0 38	0 34	0 13-0 40	0 28
Gravel (medium)	-	-	0 17-0 44	0 24
Gravel (coarse)	0 24-0 36	0 28	0 13-0 25	0 21
Silt	0 34-0 51	0 45	0 01-0 39	0 20
Clay	0 34-0 57	0 42	0 01-0 18	0 06
Limestone	0 07-0 56	0 30	–0-0 36	0 14
Wind-laid material				
Loess	-	-	0 14-0 22	0 18
Eolian sand	-	-	0 32-0 47	0 38
Tuff	-		0 02-0 47	0 21
Igneous rock				
Weathered granite	0 34-0 57	0 45	-	-
Weathered gabbro	0 42-0 45	0 43	-	-
Basalt	0 03-0 35	0 17	-	-
Metamorphic rock				
Schist	0 04-0 49	0 38	0 22-0 33	0 26

Source Data from McWorter and Sunada (1977)

Distribution coefficients depend strongly on soil type, the pH and Eh of the soil, and the presence of other ions (see Tables E 4 through E 6) Thus, considerable uncertainty can be introduced by using default values for the distribution coefficients This uncertainty is a critical matter, particularly in cases in which the water-dependent pathways are the dominant contributors to the total dose/source concentration ratios Default values for the distribution coefficients are provided only for the purpose of obtaining preliminary estimates, site-specific values should be used for deriving soil guidelines whenever possible

In addition to the option of using default values, four other options have been implemented in RESRAD to derive distribution coefficients when site-specific data are not available The first option is to derive the distribution coefficients from the soil-to-plant transfer coefficients by using the correlation proposed by Sheppard and Sheppard (1989) The second option uses the groundwater concentration data, if available, to derive the distribution coefficients The third option uses leach rate data, if available, to derive the distribution coefficients The fourth option uses solubility limit data to derive an equivalent distribution coefficient The first three options are discussed in detail in Appendix H, the fourth option is presented in Appendix J

The distance from the ground surface to the water table, $D_{wt}(t)$, at time t is

$$D_{wt}(t) = C_d(t) + T(t) + \sum_{m=1}^{n+1} \Delta z_m \, , \qquad \text{(E 23)}$$

where

$\quad C_d(t) =$ cover depth at time t (m),

$\quad T(t) =$ thickness of contaminated zone at time t (m), and

$\quad \Delta z_m$ is as defined in Equations E 20 and E 21

In the current version of RESRAD, the water table is assumed to be below the contaminated zone, that is, $D_{wt}(0) \geq C_d(0) + T(0)$

E.3.1.2 Rise Time

When the well is located at the downgradient edge of the contaminated zone, as shown in Figure E 1 (i e , if the ND model is used), the rise time is given by the formula

$$
\begin{aligned}
\delta t_{t1} &= \tau_t, & \zeta \leq d_w, \; D_{wt}(t) \geq C_d(t) + T(t) \\
&= \tau_t/(\zeta/d_w), & \zeta > d_w, \; D_{wt}(t) \geq C_d(t) + T(t) \qquad \text{(E 24)} \\
&= 0, & \zeta > d_w, \; D_{wt}(t) < C_d(t) + T(t) \, ,
\end{aligned}
$$

where

$\qquad \zeta = (1/V_{wfr})t =$ distance from the water table to the
lower boundary of contamination in the aquifer at

Contaminated Inflow

I

Well

Water
Table

Contaminated
Water

Uncontaminated
Inflow

d_w

Uncontaminated
Water

V_{wfr}

ℓ

ζ
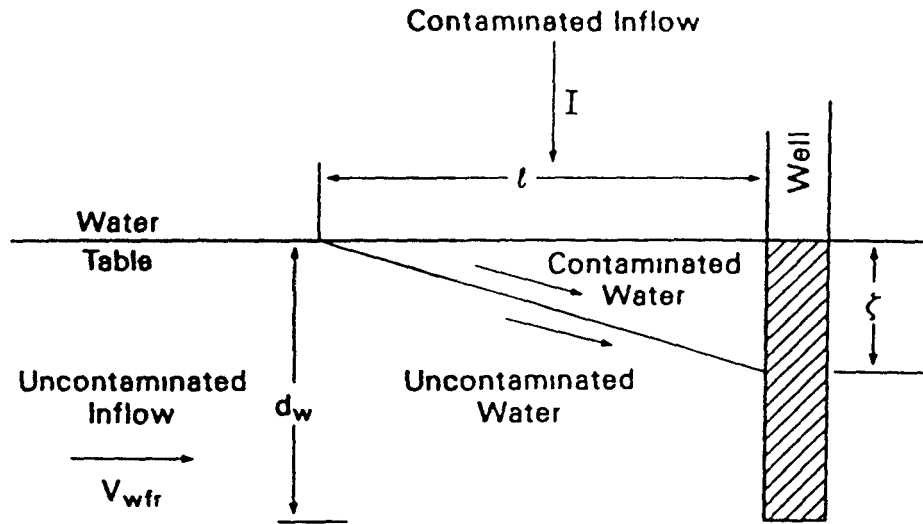
FIGURE E.1 Dilution of Contaminated Inflow by Uncontaminated Inflow in the Nondispersion Model for a Well Adjacent to the Contaminated Area

the downgradient edge of the contaminated zone (m),

I = infiltration rate (m/yr),

$V_{wfr} = K_s^{(sz)} J_x$ = water flow rate in the saturated zone (m/yr),

$K_s^{(sz)}$ = saturated hydraulic conductivity of the saturated zone (100 m/yr),

J_x = hydraulic gradient in the flow (x) direction (0 02, dimensionless),

ℓ = length of the contaminated zone parallel to the hydraulic gradient (maximum distance from the upgradient edge to downgradient edge parallel to the hydraulic gradient, 100 m),

d_w = distance of the well intake below the water table (10 m),

22

$$\tau_{\ell_i} = P_e^{(sz)} R_{d_i}^{(sz)} \ell/V_{wfr}$$ = time for the ith principal radionuclide to be transported from the upgradient edge to the downgradient edge of the saturated zone (yr),

$P_e^{(sz)}$ = effective porosity of the aquifer (0 2, dimensionless), and

$R_{d_i}^{(sz)}$ = retardation factor for the ith principal radionuclide in the saturated zone (dimensionless)

Equation E 24 is used only in the ND model   Representative porosities are given in Table E 7   The infiltration rate is given by Equation E 4   Representative saturated hydraulic conductivities are given in Table E.2.   Representative distribution coefficients are given in Tables E 3 through E 6

If the well is in the center of the contaminated zone (i e , if the MB model is used), the rise time is assumed to be zero   That is, for the MB model,

$$\delta t_{i1} = 0 \qquad\qquad\qquad (E 25)$$

E.3.1.3 Dilution Factor

It is assumed that the water flow is vertically downward from the bottom of the contaminated zone to the water table, hence, no dilution will occur in the unsaturated zone   The dilution in the saturated zone is estimated by using the conservative assumption that the dispersivity is zero

The dilution factor for the MB model is a radionuclide-independent factor given by the formula

$$f_1 = \frac{A\,I}{U_w}, \qquad\qquad A\,I < U_w \qquad\qquad (E 26)$$
$$= 1, \qquad\qquad A\,I \geq U_w ,$$

where

A = area of the contaminated zone (m^2),

I = infiltration rate (m/yr), and

U_w = well pumping rate = annual volume of water withdrawn from well (250 m^3/yr)

The infiltration rate is calculated by Equation E 4

For a well located at the downgradient edge of the contaminated zone, the dilution factor for the ND model is given by the formula

$$
\begin{aligned}
f_{i1} &= \frac{\zeta}{d_w} & d_r \leq \frac{A}{\ell}\,,\ \zeta < d_w \\[2em]
&= \frac{A\,I}{U_w} & d_r > \frac{A}{\ell}\,,\ \zeta < d_w \\[2em]
&= 1\,0 & d_r \leq \frac{A}{\ell}\,,\ \zeta \geq d_w \\[2em]
&= \frac{A\,I\,d_w}{U_w\,\zeta} & d_r > \frac{A}{\ell}\,,\ \zeta \geq d_w\,,
\end{aligned}
\tag{E 27}
$$

where d_r is the effective pumping diameter (m) and is calculated as

$$
d_r = \frac{U_w}{V_{wfr}\,d_w}
\tag{E 28}
$$

Parameters used in Equations E 27 and E 28 are defined the same as those in Equations E 24 and E 26

The dilution factors for a well that is located away from the edge of the contaminated zone can be significantly smaller than the dilution factors estimated by Equations E 26 and E 27 for a well located in or immediately adjacent to the contaminated zone The one-dimensional model used to obtain Equations E 26 and E 27 cannot be used to estimate this reduction, a two- or three-dimensional model must be used to estimate a more realistic dilution factor In addition, the assumption of no dispersivity may be unnecessarily

conservative if the well is not located very close to the contaminated zone The estimation of off-site well concentrations is discussed further in Appendix K.

E.3.2 Surface Water Pathway ($r = 2$)

The surface water pathway will consist of an on-site groundwater pathway segment that extends to the edge of the contaminated zone, an off-site groundwater pathway segment that extends from the edge of the contaminated zone to a location where surface seepage occurs, and a surface water segment in which the contaminated groundwater is mixed with uncontaminated surface water Contamination of the surface water can also occur as a consequence of erosion as contaminated soil is deposited in a nearby streambed or pond This pathway is not included in the current version of RESRAD

E.3.2.1 Breakthrough Time

The breakthrough time for the surface water pathway is assumed to be the same as that for the groundwater pathway, that is,

$$\Delta t_{i2} = \Delta t_{i1} = \Delta t_i \, , \qquad \text{(E 29)}$$

where Δt_i is calculated by using Equations E 19 through E.22

E.3.2.2 Rise Time

The rise time for the surface water pathway is assumed to be the same as that used in the ND model for the groundwater pathway, that is,

$$\delta t_{i2} = \delta t_{i1} \, , \qquad \text{(E 30)}$$

where δt_{i1} is given by Equation E 24

E.3.2.3 Dilution Factor

The dilution factor for the surface water pathway is based on the assumption that the surface water is a pond and (1) the inflow and outflow for the pond are in steady-state equilibrium and (2) the annual inflow of radioactivity into the pond is equal to the annual quantity of radioactivity leached from the contaminated zone With these assumptions, the

dilution factor is the ratio of the annual volume of water that percolates through the contaminated zone to the annual total inflow of water into the pond If, in addition, it is assumed that the infiltrating water flow is vertically downward, the dilution factor is given by the formula

$$f_2 = A/A_w ,$$

(E 31)

where

    A = area of contaminated zone (10^4 m^2), and

    A_w = area of watershed (10^6 m^2)

E.4 REFERENCES

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APPENDIX H

DISTRIBUTION COEFFICIENTS

The distribution coefficient, K_d, is a partitioning coefficient under equilibrium conditions that assumes a linear relationship between the concentration of a solute in the solid (S) and the liquid (C) phases, that is, $S = K_d C$ This model implicitly assumes that the dissolution of radionuclides is not limited by the solubility limit The solubility limit model is discussed in Appendix J The value of K_d for different radionuclides is quite variable, depending strongly on soil type, the pH and Eh of the soil, and the presence of other ions Thus, considerable uncertainty can be caused by using default values for the distribution coefficient, especially when the water-dependent pathways are the dominant factors in the dose/source concentration ratios Therefore, site-specific values should always be used whenever they are available The measurement methodology for the distribution coefficients is discussed in the RESRAD Data Collection Handbook (Yu et al 1993)

In addition to the direct input of K_d values from the screen, RESRAD provides four optional methods for deriving the distribution coefficient The first method requires inputting a greater than zero value for the elapsed time since material placement (TI) and providing the groundwater concentration of the radionuclide, which is measured at the same time as the radionuclide soil concentration The second method uses the input solubility limit to derive an effective K_d The third method uses the nonzero input leach rate (default is 0) to derive K_d The last method is based on the correlation between the plant/soil concentration ratio and the water/soil distribution coefficient, which can be invoked by setting the K_d value to -1 on the input screen Only one of the four methods can be used in each RESRAD execution. If more than one of the requirements is satisfied, RESRAD will always choose according to the following order — the groundwater concentration method first, the solubility limit method second, the leach rate method third, and the plant/soil concentration ratio method last The solubility limit method is described in Appendix J, the other three methods are discussed below

H.1 GROUNDWATER CONCENTRATION METHOD

The groundwater concentration method requires inputting two parameters — the elapsed time since material placement (*TI*) and the groundwater concentration (W_i) for radionuclide i The values for both parameters should be greater than zero The radionuclide groundwater concentration is measured in an on-site well at the same time as the soil concentration is measured The well is assumed to be located at the downgradient side of the site boundary for the nondispersion (ND) model (see Appendix E) For the mass balance (MB) model, in which the well is located at the center of the site, the groundwater input method is not applicable

On the basis of measured soil and groundwater concentrations and the elapsed time between the disposal of radioactive wastes and the performance of a radiological survey, it is possible to determine the distribution coefficient of a radionuclide with the provided geological and geometrical information To simplify the derivation procedures, it is assumed that the distribution coefficients of radionuclide i in the contaminated zone, $K_{d_i}^{(cz)}$, in the unsaturated zone, $K_{d_{im}}^{(uz)}$, and in the saturated zone, $K_{d_i}^{(sz)}$, are equal The geological and geometrical structure of the contaminated site is assumed to be unchanged between the time of the waste placement and the performance of the radiological survey, that is, the thickness of the cover material and the contaminated zone and the distance from the ground surface to the water table remain the same. Iterative calculations to find a best fit value for the distribution coefficient can then be carried out following the leaching model presented in Appendix E

During the calculational iteration, input data are checked constantly for the possibility of finding a reasonable K_d to match the specified environmental setting If RESRAD finds that the input data violate the leaching model, thus making the derivation of a reasonable K_d impossible, warning messages will appear on the screen, and the input groundwater concentration will be reset to zero The default value of K_d can then be used to continue the remaining calculations This case leads to the same result as if no groundwater contamination had been observed during the radiological survey The user is advised to check the input value of *TI* or the groundwater concentration in the next RESRAD execution so that a reasonable K_d can be derived Since the K_d value of only one radionuclide is solved in each iteration, when a decay chain of more than one principal radionuclide is

involved, the K_d values for the other radionuclides will be used in the iteration For example if uranium-238 and uranium-234 exist in the contaminated soil, and the groundwater con centrations for both radionuclides are detected, then the K_d value of uranium-238 will be used in the iteration procedure for uranium-234 Because of the listing order of principal radionuclides in the RESRAD code, the iteration procedure for uranium-234 will be performed first, so that the K_d value for uranium-238 used in the iteration is obtained from the user input file rather than from an iteration procedure This may result in an inaccurate K_d for uranium-234, if the input K_d for uranium-238 is inaccurate To reduce such inaccuracy, it may be necessary to run RESRAD several times to obtain the correct values In the repeated runs, the groundwater concentrations of each radionuclide are assigned sequentially according to the decay order In the first run, only the first radionuclide in the decay chain is input with a nonzero groundwater concentration For the second run, the derived K_d for the first radionuclide is used, and the groundwater concentration of the second radionuclide in the decay chain is added (the groundwater concentration of the first radionuclide can either be set to zero or carried over from the first run) This procedure can be used for the remainder of the radionuclides in the decay chain Sections H.1 1 and H 1 2 detail the iteration procedure used in RESRAD for deriving distribution coefficients by the groundwater concentration method

H.1.1 Breakthrough Time and Rise Time as Functions of K_{d_i}

According to Equations E 19 and E 21, the breakthrough time for radionuclide i can be written as

$$\Delta t_i = \frac{\sum_{m=1}^{n+1} \Delta Z_m \, R_{d_{im}}^{(uz)} \, P_{e_m}^{(uz)} \, R_{s_m}^{(uz)}}{I} \tag{H 1}$$

Substituting $R_{d_{im}}^{(uz)}$ with Equation E.22, Δt_i then becomes

$$\Delta t_i = \frac{\sum_{m=1}^{n+1} \Delta Z_m P_{e_m}^{(uz)} R_{s_m}^{(uz)} \left[1 + \frac{\rho_{b_m}^{(uz)} K_{d_i}^{(uz)}}{P_{t_m}^{(uz)} R_{s_m}^{(uz)}} \right]}{I} \qquad (H\,2)$$

Equation H.2, after rearrangement, can be expressed as a linear function of K_{d_i},

$$\Delta t_i = X_1 + X_2 K_{d_i} \quad , \qquad (H\,3)$$

where

$$X_1 = \frac{\sum_{m=1}^{n+1} \Delta Z_m P_{e_m}^{(uz)} R_{s_m}^{(uz)}}{I} \quad , \qquad (H\,4)$$

and

$$X_2 = \sum_{m=1}^{n+1} \frac{\Delta Z_m P_{e_m}^{(uz)} \rho_{b_m}^{(uz)}}{P_{t_m}^{(uz)} I} \qquad (H\,5)$$

The rise time, δt_i, depends on the geometrical characteristics of the site For the MB model, the value of δt_i equals 0 because the well is located at the center of the contaminated zone For the nondispersion model, δt_i is a function of τ_{t_i} and can be expressed as

$$\delta t_i = (\tau_{t_i}) \chi \qquad (H\,6)$$

The value of χ, according to Equation E.24, is

$$\chi = \begin{array}{llll} 1 & \zeta \leq d_w \, , & D_{wt}(t) \geq C_d(t) + T(t) \\ 1/(\zeta/d_w) & \zeta > d_w \, , & D_{wt}(t) \geq C_d(t) + T(t) \\ 0 & \zeta > d_w \, , & D_{wt}(t) < C_d(t) + T(t) \end{array} \qquad (H\,7)$$

By incorporating the definition of τ_{t_i} into Equation H 6, δt_i then can be written as

$$\delta t_\iota = \left[\frac{P_e^{(sz)} \, R_{d_\iota}^{(sz)} \, l}{V_{wfr}} \right] \chi \qquad \text{(H 8)}$$

$$= \left[\frac{P_e^{(sz)} \, l}{V_{wfr}} \right] \chi \; + \; \left[\frac{P_e^{(sz)} \, l \, \rho_b^{(sz)}}{V_{wfr} \, P_t^{(sz)} \, R_s^{(sz)}} \right] \chi \, K_{d_\iota} \qquad \text{(H 9)}$$

$$= X_3 \; + \; X_4 \, K_{d_\iota} \quad , \qquad \text{(H 10)}$$

where

$$X_3 = \left[\frac{P_e^{(sz)} \, l}{V_{wfr}} \right] \chi \qquad \text{(H 11)}$$

and

$$X_4 = \left[\frac{P_e^{(sz)} \, l \, \rho_b^{(sz)}}{V_{wfr} \, P_t^{(sz)}} \right] \chi \qquad \text{(H 12)}$$

because

$$R_s^{(sz)} = 1 \qquad \text{(H 13)}$$

The leach rate constant L_ι for radionuclide ι is also a function of K_{d_ι}. From Equation E 3, L_ι can be expressed as

$$L_\iota = \frac{1}{X_5 + X_6 \, K_{d_\iota}} \qquad \text{(H 14)}$$

with

$$X_5 = \frac{P_t^{(cz)} \, R_s^{(cz)} \, T(t)}{I} \qquad \text{(H 15)}$$

and

$$X_6 = \frac{T(t) \, \rho_b^{(cz)}}{I} \qquad \text{(H 16)}$$

H.1.2 Solution for the Distribution Coefficient

H.1.2.1 Relationship between the Water/Soil Concentration Ratio and the Distribution Coefficient

For a principal radionuclide that is not a decay product of any other radionuclide, the relationship between the water/soil concentration ratio [the ratio of water concentration at time t to the input soil concentration, $W_i(t)/S_i(0)$] and the distribution coefficient (K_{d_i}) is such that for a contaminated site with a specific geological structure, an increase in K_{d_i} will result in an increase in the breakthrough time Δt_i and the rise time δt_i, but will result in a decrease in the leach rate constant (L_i), therefore, the maximum value of $W_i(t)/S_i(0)$ will decrease When the principal radionuclide i is a decay product of other radionuclides, the times to observe the beginning of a nonzero water/soil concentration ratio $W_i(t)/S_i(0)$ and its maximum are not necessarily Δt_i and $\Delta t_i + \delta t_i$, respectively These times depend not only on the K_d of nuclide i but also on the K_d's of its parent radionuclides It is difficult to define precisely the magnitude range of the distribution coefficient K_{d_i} based on a measured groundwater concentration W_i To make it simpler, the range of K_{d_i} is defined by considering radionuclide i independently, that is, the range is the same as that for a radionuclide that does not originate from the decay of other radionuclides Although this assumption is inaccurate, for the possible values of *TI* (which are always less than 100) in most cases, the defined range is a good approximation and includes the final solution After the range is defined, an iteration procedure is used to find a best fit value for K_{d_i} An internal absolute time frame is used in the calculation of the water/soil concentration ratio, that is, the origin $t = 0$ corresponds to the time the contaminants were placed on-site Whenever the input *TI* is greater than 0, RESRAD will calculate the soil concentrations of all principal radionuclides at the placement time The ratios of water concentrations at different times with the measured soil concentrations are then calculated The iteration procedure will find a best fit value of K_{d_i}, so that at time *TI*, the water/soil concentration ratio is the measured value of $(W_i/S_i)_m$ The derived K_{d_i} will result in a *TI* that is greater than the corresponding breakthrough time (Δt_i) and smaller than the corresponding rise time $(\Delta t_i + \delta t_i)$

H.1.2.2 Definition and Magnitude Range of the Distribution Coefficients

The various distribution coefficients used in the iterative calculation based on the groundwater concentration method are defined as follows

$(K_{d_i})_r$ — The distribution coefficient of radionuclide i that causes the maximum water/soil concentration ratio to occur at time *TI* (absolute time frame)

$(K_{d_i})_{bt}$ — The distribution coefficient of radionuclide i that causes the breakthrough time to equal *TI* (absolute time frame)

The solution of the distribution coefficient for radionuclide i, K_{d_i}, can be found only for the ND model The distribution coefficient $(K_{d_i})_r$ that has its peak at *TI* should be the lower limit for K_{d_i} The preliminary requirement for observing any concentration in groundwater is that the absolute time *TI* must be equal to or greater than the breakthrough time Δt_i Thus $(K_{d_i})_{bt}$ is the upper limit for K_{d_i}

H.1.2.3 Calculation of $(K_{d_i})_r$ and $(K_{d_i})_{bt}$

From the above discussion, if the distribution coefficient for radionuclide i is $(K_{d_i})_r$, then the peak of the water/soil concentration ratio will occur at time *TI* (absolute time) On the basis of this information, $(K_{d_i})_r$ can then be solved by

$$TI = \Delta t_i + \delta t_i \tag{H 17}$$

$$= (X_1 + X_3) + (X_2 + X_4)(K_{d_i})_r \tag{H 18}$$

Therefore,

$$(K_{d_i})_r = \frac{TI - (X_1 + X_3)}{X_2 + X_4} \tag{H 19}$$

The water/soil concentration ratio, $(W_i(t)/S_i(0))_r$, calculated at time *TI* (absolute time) with $(K_{d_i})_r$ will be greater than (or equal to) the measured value $(W_i/S_i)_m$ The value of $(K_{d_i})_{bt}$ can easily be solved by setting *TI* to Δt_i

$$TI = \Delta t_i \qquad \text{(H 20)}$$

$$= X_1 + X_2 \, (K_{d_i})_{bt} \qquad \text{(H 21)}$$

$$(K_{d_i})_{bt} = \frac{(TI - X_1)}{X_2} \qquad \text{(H 22)}$$

Because, by definition, the distribution coefficient K_{d_i} should always be greater than or equal to zero, any negative solution for $(K_{d_i})_{bt}$ is not allowed The occurrence of a negative $(K_{d_i})_{bt}$ indicates that no contamination of radionuclide i should be observed at time TI (absolute time) in accordance with the specified geological structure of the site, because the elapsed time TI is shorter than the breakthrough time Δt_i, this is obviously contrary to the observation Therefore, if the calculated $(K_{d_i})_{bt}$ is less than zero, a warning message will appear on the screen, and the water concentration will be neglected
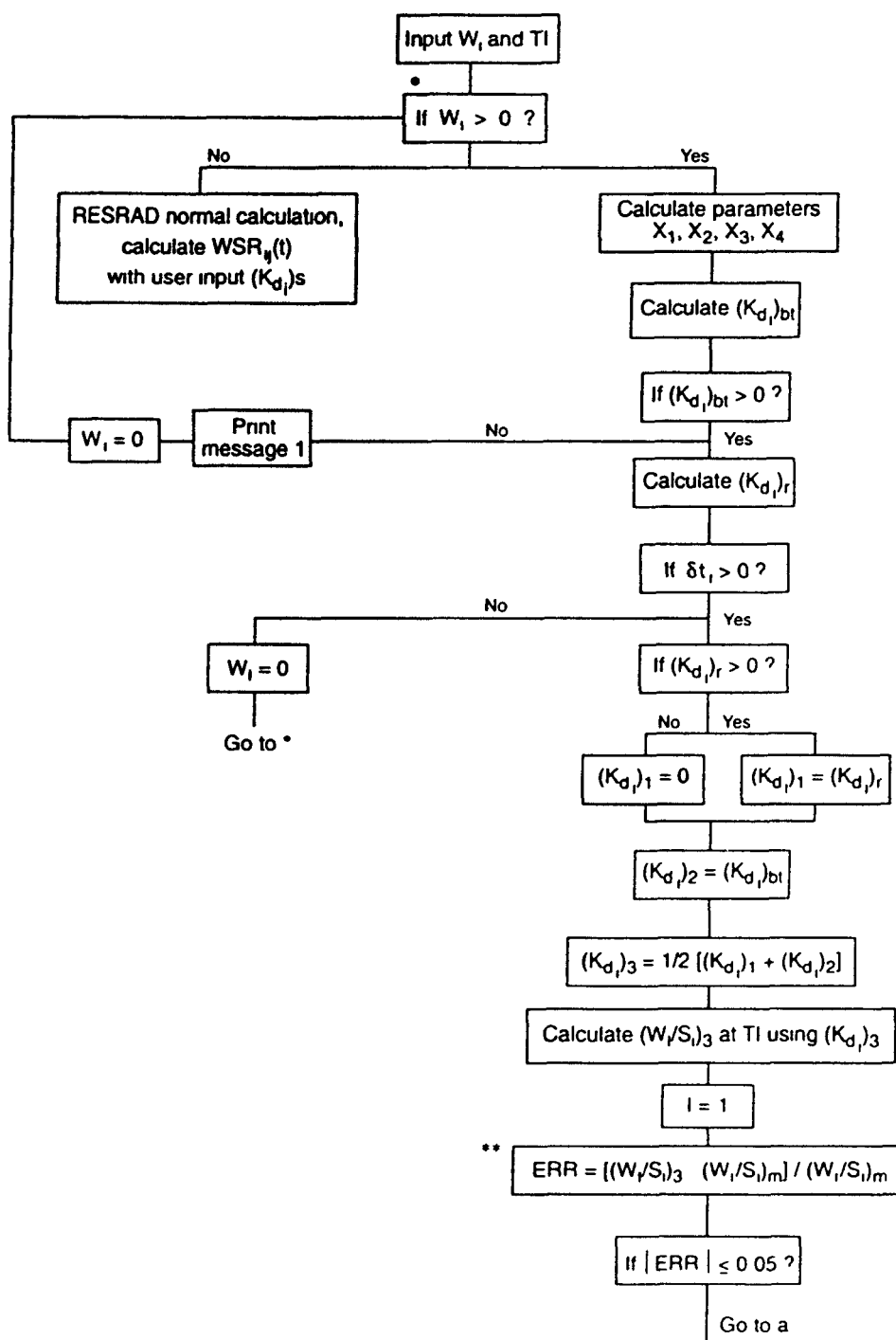
H.1.2.4 Flow Diagram for the Iteration Procedure

Once the magnitude range for K_{d_i} is solved, an iterative calculation is performed to solve for K_{d_i} A preliminary check must be made, however, to make sure that it is possible to find a solution When $(K_{d_i})_{bt}$ is less than 0, a warning message will appear on the screen and the iteration will be aborted The normal calculation will be continued by setting W_i to 0 and using the default or input distribution coefficient Figure H 1 illustrates the flow diagram for the iteration procedure

H.2 THE LEACH RATE METHOD

When a nonzero leach rate for radionuclide j[1] is input, RESRAD will calculate the distribution coefficient on the basis of this value Equation E 3 is used first to derive the retardation factor for the contaminated zone, then Equation E 8 is used to obtain K_d, the distribution coefficient of the contaminated zone After K_d is obtained, its magnitude will be checked for validity (K_d must be greater than or equal to 0) If K_d is negative, indicating that

---

[1] The index j corresponds to principal radionuclides present originally as well as any principal radionuclides resulting from ingrowth

Input W_i and TI

If $W_i > 0$?

No → RESRAD normal calculation, calculate $WSR_{ij}(t)$ with user input (K_{d_i})s

Yes → Calculate parameters X_1, X_2, X_3, X_4

Calculate $(K_{d_i})_{bt}$

If $(K_{d_i})_{bt} > 0$?

$W_i = 0$

Print message 1

No →

Yes → Calculate $(K_{d_i})_r$

If $\delta t_i > 0$?

No →

$W_i = 0$

Go to •

Yes → If $(K_{d_i})_r > 0$?

No → $(K_{d_i})_1 = 0$

Yes → $(K_{d_i})_1 = (K_{d_i})_r$

$(K_{d_i})_2 = (K_{d_i})_{bt}$

$(K_{d_i})_3 = 1/2 [(K_{d_i})_1 + (K_{d_i})_2]$

Calculate $(W_f/S_i)_3$ at TI using $(K_{d_i})_3$

$I = 1$

** ERR $= [(W_f/S_i)_3 \quad (W_i/S_i)_m] / (W_i/S_i)_m$

If $|ERR| \leq 0\ 05$?

Go to a

Message 1   With the input information it is impossible to observe a nonzero concentration of radionuclide i in groundwater Calculation resumes by setting the groundwater concentration of radionuclide i to 0

FIGURE H 1   Flow Diagram for the Iterative Calculations

36

a

No ─────────────────────────────────── Yes

If $(W_i/S_i)_3 > (W_i/S_i)_m$? $K_{d_i} = (K_{d_i})_3$

No ──────────────── Yes

$(K_{d_i})_2 = (K_{d_i})_3$ $(K_{d_i})_1 = (K_{d_i})_3$

$(K_{d_i})_3 = 1/2 \, [(K_{d_i})_1 + (K_{d_i})_2]$

Calculate $(W_i/S_i)_3$ at TI using $(K_{d_i})_3$

$I = I + 1$

Is $I > 30$?

No │   Yes

Go to ** $K_{d_i} = 0$

If $(K_{d_i}) = 0$?

No ───────────────────── Yes

$K_{d_i} (cz) = K_{d_i}, \; K_{d_i} (sz) = K_{d_i}$ Print
$K_{d_i} (uz) = K_{d_i}, \; 1 \leq m \leq n+1$ message 2

End of iteration $W_i = 0$

RESRAD normal calculation,   Go to *
calculate $WSR_{ij}(t)$
with obtained (K_{d_i})s
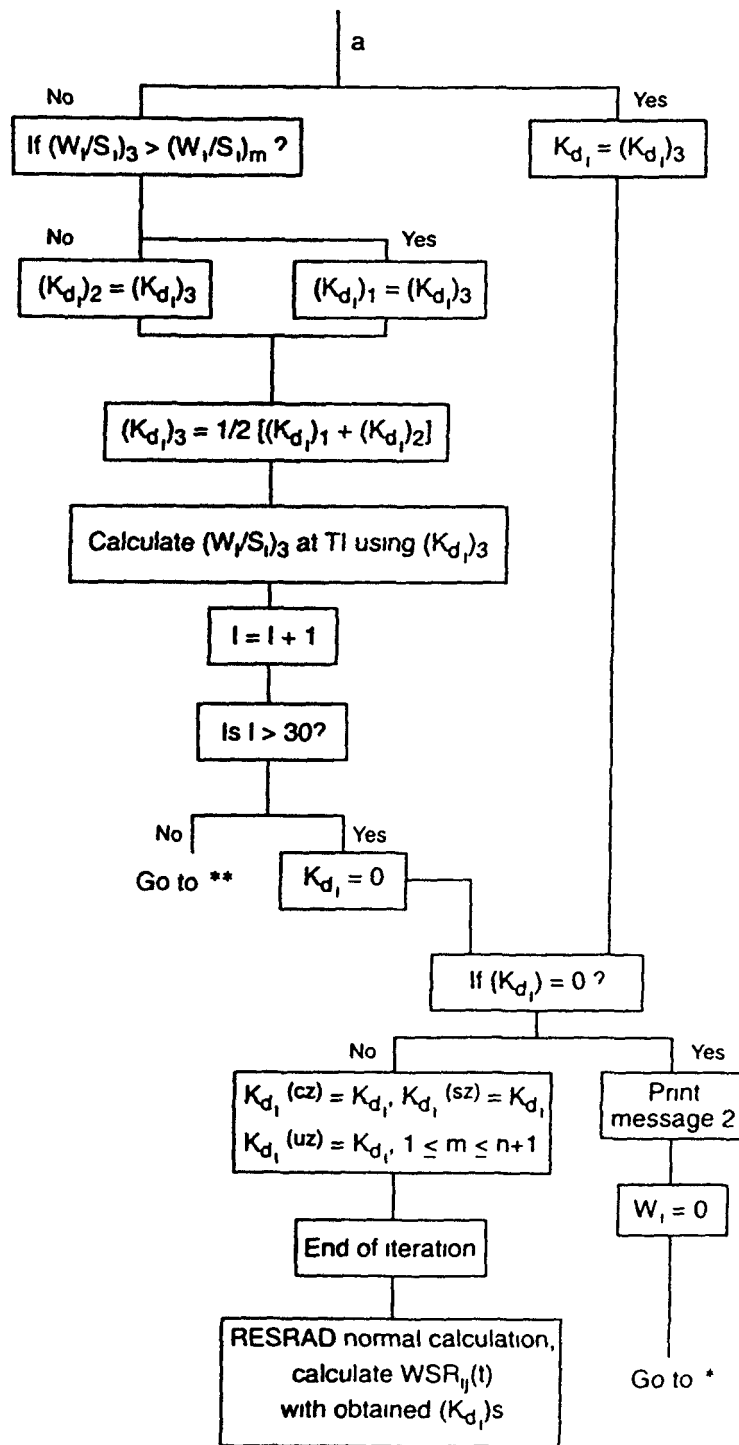
Message 2
Iteration without convergence Calculation resumes by setting the groundwater concentration of radionuclide i to 0

FIGURE H 1 (Cont)

the input leach rate is unreasonably large according to the leaching model in Appendix E, then the input leach rate will be neglected, and its value will be recalculated with the input or default distribution coefficient This process results in the same situation as if the input leach rate of radionuclide *j* were zero Otherwise, the derived K_d will replace the screen input value and RESRAD will continue the remaining calculations

When an acceptable K_d is derived, this value will be used not only for the contaminated zone but for the unsaturated zone(s) and the saturated zone If the user does not want to have the input distribution coefficients of the unsaturated zone(s) and the saturated zone substituted, another execution of RESRAD with the derived K_d for the contaminated zone and a zero input leach rate is required

H.3 THE PLANT/SOIL CONCENTRATION METHOD

Another method for deriving the distribution coefficient is the plant/soil concentration method According to Baes et al (1984) and Sheppard and Sheppard (1989), a strong correlation exists between the plant/soil concentration ratio (*CR*) and the contaminated zone distribution coefficient K_d Sheppard and Thibault (1990) proposed the following correlation equation

$$\ln K_d = a + b \, (\ln CR) \ , \tag{H 23}$$

where *a* and *b* are constants From experimental data, the value for the coefficient *b* is found to be -0 5 The value of *a* depends on soil type for sandy soil, $a = 2\,11$, for loamy soil, $a = 3\,36$, for clayey soil, $a = 3\,78$, and for organic soil, $a = 4\,62$ Baes et al (1984) also proposed the above correlation equation (Equation H 23), however, with different coefficient values Equation H 23 provides a method to estimate the distribution coefficient from the plant/soil concentration ratio, especially when experimental or literature data are not available

The plant/soil concentration ratio (*CR*) used is based on the weights of dry soil and wet plants The soil-to-plant transfer coefficient, B_{jv}, used in RESRAD is also based on the weights of dry soil and wet plants Therefore, the RESRAD default B_{jv} values or the user-specified values of the soil-to plant transfer factors can be used in Equation H 23 for the calculation of K_d,

$$\ln K_{d_j} = a + b \ (\ln B_{jv}) \ , \tag{H 24}$$

where j is the radionuclide index   When the input distribution coefficient K_d value (whether it is for the contaminated, unsaturated, or saturated zone) is -1, the soil-to-plant transfer factor B_{jv} will be used for calculating the distribution coefficients by using Equation H 24 In the current version of RESRAD, loamy soil is assumed, that is, $a = 3\ 36$ in Equation H 24 It is also assumed that the derived K_d applies to all zones If the user would like to use different K_d values for different soil layers, then RESRAD must be executed once again with the derived value assigned to the proper soil layer

H.4 REFERENCES

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Sheppard, M I , and Thibault, D H , 1990, "Default Soil Solid/Liquid Partition Coefficients, K_ds, for Four Major Soil Types   a Compendium," *Health Physics* 59 471-482

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APPENDIX J

ESTIMATION OF THE DISTRIBUTION COEFFICIENT
ON THE BASIS OF THE SOLUBILITY CONSTANT

J.1 INTRODUCTION

The present leaching model in the RESRAD code requires the input of an empirical distribution coefficient, K_d, which represents the ratio of the solute concentration in soil to that in solution under equilibrium conditions Parameters that affect the measurement of the distribution coefficient are the physical and chemical characteristics of the soil and the chemical species present in the contact solution For soils contaminated with radionuclides, the radionuclides may be associated with particulate matter in several chemical forms, resulting in differences in leachability and solubility When in contact with chemical species in solution, these radionuclides might be desorbed into the solution phase, possibly by dissolution or complexation Therefore, the investigation of radionuclide distribution among different geochemical species and the solubility of these geochemical species will be useful for predicting the possible maximum concentration of a radionuclide in soil solution The estimated maximum radionuclide concentration in soil solution can be further utilized to calculate the distribution coefficient under more conservative conditions for modeling purposes The methodology for estimating the distribution coefficient on the basis of radionuclide solubility is presented, and sample calculations are provided to demonstrate the use of this methodology

J.2 METHODOLOGY

In the earliest stage of the leaching process, geochemical species with high solubilities are first released into the solution phase by dissolution As leaching proceeds, geochemical species with low solubilities will start to dissolve The investigation of radionuclide distribution among different geochemical species can provide useful information for predicting the radionuclide concentration under equilibrium desorption conditions Unfortunately, laboratory information on possible solid phase and solution species of radionuclides is usually unavailable, and the little information that is available is mostly very site- and solution-specific, making extrapolation of data very difficult To estimate the possible solids present in a given soil solution system, available thermodynamic data were

40

used to construct Eh-pH diagrams (Garrels and Christ 1965, Pourbaix 1966) and activity-pH diagrams (Rai and Lindsay 1975; Rai and Serne 1977) Ames and Rai (1978) reported that although Eh-pH diagrams can be used to predict the presence of different solids for elements that exist in more than one oxidation state, these diagrams do not indicate the total amount of the element and the relative amount of various species in solution under specific conditions Therefore, activity-pH diagrams were used

J.2.1 Activity-pH Diagrams for Radionuclides

The methodology used for developing a stability and/or activity-pH diagram utilizes thermodynamic standard free energies of formation ($\Delta G_f{}^\circ$) to calculate equilibrium constants for various minerals/solids under standard conditions, that is, 1 atm and 25°C On the basis of the estimated equilibrium reaction constant, the equation for the activities of related chemical species in a specific mineral or solid can be formulated For any given soil solution system for which there is insufficient chemical information, activities of common cations (such as Ca^{+2}, Mg^{+2}, K^+, Na^+, etc) and anions (such as Cl^-, HCO_3^-, CO_3^{-2}, NO_3^-, F^-, SO_4^{-2}, and PO_4^{-3}) are usually selected to represent expected environmental conditions The equation for the activity of the radionuclide being investigated can then be simplified to be a function of the solution pH For each radionuclide investigated, the stability diagram can be constructed so as to provide information on the saturate solubility of the radionuclide under given environmental conditions with different solution pHs Typical soil concentrations of selected elements and inorganic anions have been reported by Rai and Lindsay (1975), Dvorak et al (1978), and Nieto and Frankenberger (1985) For sites with specific soil solution properties, the stability diagram can be modified to correspond to the actual ionic activities This modification would result in an upward or downward shift of the isotherms Rai and Lindsay (1975) used Al-minerals, such as analcime ($NaAlSi_2O_6\ H_2O$), to present the details of the method for constructing stability diagrams

Chemical information on contaminated soils and contact solutions is needed for an accurate prediction of possible reactions in the soil-solution system To aid in estimating the possible solution composition under typical environmental conditions, stability diagrams available in the literature are reviewed Stability diagrams are summarized in Section J 4 for some of the radionuclides considered in the current version of RESRAD

J.2.2 Estimation of the Saturate Solubility for a Specific Radionuclide

Consider a soil-solution system in which the initial concentration of radionuclide ι in soil is $S_\iota(0)$ (pCi/g soil). Assume that all of radionuclide ι can be released into the soil solution under the worst desorption conditions, the total activity of radionuclide ι in this soil solution system $C_{tot,\iota}$ (mol/L) is

$$C_{tot,\iota} = S_\iota(0) \times M_s \times \frac{1}{SA_\iota} \times \frac{1}{AW_\iota} \times \frac{1}{V_{solution}} \times \frac{1,000\,\text{mL}}{\text{L}} , \qquad (\text{J 1})$$

where

$\quad Ms \quad\quad = \quad$ total mass of contaminated soil (g),

$\quad\quad\quad\quad\quad = \quad$ volume of contaminated soil $\times$ bulk density of soil,

$\quad\quad\quad\quad\quad = \quad V \times \rho_b,$

$\quad V_{solution} \quad = \quad$ volume of soil solution (mL),

$\quad\quad\quad\quad\quad = \quad$ volume of contaminated soil $\times$ total porosity $\times$ saturation ratio,

$\quad\quad\quad\quad\quad = \quad V \times p_\iota \times R_s,$

$\quad SA_\iota \quad = \quad$ specific activity of radionuclide ι (pCi/g),

$\quad AW_\iota \quad = \quad$ atomic weight of radionuclide ι (g/mole),

and

$$C_{tot,\iota} = S_\iota(0) \times \frac{\rho_b}{p_\iota R_s} \times \frac{1}{SA_\iota} \times \frac{1}{AW_\iota} \times 1,000 \left(\frac{\text{mol}}{\text{L}}\right) \qquad (\text{J 2})$$

In the stability diagram of radionuclide ι, any solid with its stability line below another solid's stability line is more stable than another solid. Thus, the maximum activity of radionuclide ι in soil solution ($C_{tot,\iota}$) in the stability diagram can be used as the starting point to search for the saturate solubility by the following process

1   In the stability diagram for radionuclide ι, draw a horizontal line L_1 with $\log A_1 = \log C_{tot\ \iota}$ to represent the total activity of radionuclide ι in

the soil solution system. Any solids with a solubility line below L_1 might be present as stable solids in the given soil solution system

2   At a specific solution pH, draw a vertical line L_2 The intercept between L_2 and the solubility line right below L_1 indicates the activity of radionuclide i in a saturate soil solution, that is, saturate solubility S_{max}, at the specific solution pH

J.2.3 Estimation of the Distribution Coefficient for Input into RESRAD

For the soil solution system discussed above, assume that, at equilibrium conditions, X fraction (%) of total activity of radionuclide i will be released into the solution phase On the basis of the radioactivity measurement, the empirical distribution coefficient K_d for radionuclide i is defined as

$$K_{d_i} = \frac{\textit{Radioactivity Remaining in Soil Phase, pCi/g soil}}{\textit{Radioactivity Released into Solution Phase, pCi/mL solution}} \qquad \text{(J 3)}$$

Then

$$K_{d_i} = \frac{S_i(0) \times (1-X) \times M_s}{M_s} \times \frac{V_{solution}}{S_i(0) \times X \times M_s} \qquad \text{(J 4)}$$

$$= \frac{1-X}{X} \times \frac{p_t R_s}{\rho_b}$$

Calculation of the distribution coefficient can be performed by using the following procedure

1   Calculate the maximum mass concentration of radionuclide i, C_{max}, on the basis of the estimated saturate solubility

$$C_{max} = S_{max} \left(\frac{\text{mol}}{\text{L}}\right) \times \frac{\text{L}}{1{,}000\,\text{mL}} \times AW_i \left(\frac{\text{g}}{\text{mol}}\right), \left(\frac{\text{g}}{\text{mL solution}}\right) \qquad \text{(J 5)}$$

$$S_{max} = \textit{Saturate Solubility}$$

2 Calculate the fraction of the total radionuclide mass released into the solution phase, X_{max}.

$$X_{max} = \frac{C_{max} \times SA_i \times V_{solution}}{S_i(0) \times M_s} \qquad (J\ 6)$$

$$= C_{max} \times \frac{SA_i}{S_i(0)} \times \frac{p_t\ R_s}{\rho_b}$$

3 Calculate the distribution coefficient

$$K_{d_i} = \frac{1-X_{max}}{X_{max}} \times \frac{p_t R_s}{\rho_b} \qquad (J\ 7)$$

J.3 SAMPLE CALCULATION

A sample calculation is summarized in this section by using uranium-238 as the principle contaminant Consider a contaminated site with the following properties

Contaminated soil

Area	1,000 m^2
Depth	1 m
Bulk density, ρ_b	1 6 g/cm^3
Total porosity, p_t	0 4
Saturation ratio, R_s	0 5

Contaminant (uranium-238)

Initial concentration	1,000 pCi/g soil
Specific activity	3 36 × 10^5 pCi/g

1 Calculate the total activity of uranium-238 in the soil solution system

44

$$C_{tot,i} = S_i(0) \times \frac{\rho_b}{p_i R_s} \times \frac{1}{SA_i} \times \frac{1}{AW_i} \times 1,000 \qquad (J\ 8)$$

$$= 1,000 \times \frac{1\ 6}{0\ 4 \times 0\ 5} \times \frac{1}{(3\ 36 \times 10^5)} \times \frac{1}{238\ 1} \times 1,000 = 0\ 1 \left(\frac{mol}{L}\right)$$

2   Estimate the saturate solubility of uranium-238 in solution   On the basis of the stability diagram for UO_2^{+2} shown in Figure J 11, draw a horizontal line L_1 with log A_i = -1 to represent the total activity of uranium-238   Draw a vertical line L_2 to represent the solution pH   The UO_2^{+2} solid with a stability line right below L_1 at each solution pH is used as the reference solid   The intercept between L_2 and the stability line of the reference solid indicates the saturate solubility of UO_2^{+2} in the soil solution system investigated   For soil solution systems with a solution pH varying from 4 to 9, the estimated saturate solubilities are listed below

Solution pH	Reference Solid	Saturate Solubility S_{max}, mol/L
4	$UO_2(OH)_2$ H_2O	4×10^{-3}
5	$UO_2(OH)_2 \cdot H_2O$	5×10^{-5}
6	$UO_2(OH)_2$ H_2O	3×10^{-7}
7	UO_2CO_3	1×10^{-3}
8	UO_2CO_3	1×10^{5}
9	UO_2CO_3	1×10^{7}

3   Calculate the distribution coefficient for each soil solution system with a different solution pH

For solution pH = 5, the distribution coefficient is calculated on the basis of the following process

a   Calculate the maximum mass concentration of uranium-238 in the soil solution as

$$C_{max} = 5 \times 10^{-5} \frac{mol}{L} \times \frac{L}{1,000\,mL} \times \frac{238\,1\,g}{mol} \tag{J 9}$$

$$= 1\,19 \times 10^{-5} \frac{g\ U\text{--}238}{mL\ solution}$$

b Calculate the maximum fraction of total uranium-238 released into the solution phase as

$$X_{max} = C_{max} \times \frac{SA_\iota}{S_\iota(0)} \times \frac{p_\iota R_s}{\rho_b} \tag{J 10}$$

$$= 1\,19 \times 10^{-5} \times \frac{3.36 \times 10^5}{1,000} \times \frac{0\,4 \times 0\,5}{1\,6} = 5 \times 10^{-4}$$

c Calculate the distribution coefficient as

$$K_{d_\iota} = \frac{1 - X_{max}}{X_{max}} \times \frac{p_\iota R_s}{\rho_b} \tag{J 11}$$

$$K_{d_\iota} = \frac{1 - (5 \times 10^{-4})}{5 \times 10^{-4}} \times \frac{0\,4 \times 0\,5}{1\,6} = 250 \left(\frac{ml}{g} \right) \tag{J 12}$$

4 The distribution coefficients, K_d, for uranium-238 in soil solution systems with different solution pHs are calculated and summarized below

Solution pH	Calculated K_d (mL/g)
4	3
5	250
6	$4\,17 \times 10^4$
7	12 38
8	$1\,25 \times 10^4$
9	$1\,25 \times 10^5$

J.4 RESRAD INPUT REQUIREMENTS

The RESRAD code provides an additional option for calculating the distribution coefficient by using the solubility constant To use this option, users need to input the solubility constant. With the input solubility constant, RESRAD will estimate a distribution coefficient corresponding to the solubility limit desorption conditions

Constants of specific activity and atomic weight for radionuclides considered in the current RESRAD database are summarized in Table J 1

J.5 COMPILATION OF STABILITY DIAGRAMS

The chemistry and geochemistry of radionuclides in RESRAD will be briefly reviewed in this section from the standpoint of the relative solubilities of possible solid phases The work summarized below is based on the assumption that radiochemical properties of all isotopes of an element are identical in respect to their reaction with geological materials

TABLE J.1 Constants of Atomic Weight and Specific Activity for Radionuclides in the Current RESRAD Database

Radionuclide	Atomic Weight (g/mol)	Specific Activity (pCi/g)	Radionuclide	Atomic Weight (g/mol)	Specific Activity (pCi/g)
Ac-227	227 1	$7\ 24 \times 10^{13}$	Ni-63	62 9	$5\ 68 \times 10^{13}$
Am 241	241 1	$3\ 42 \times 10^{12}$	Np-237	237 1	$7\ 04 \times 10^{8}$
Am 243	243 1	$2\ 00 \times 10^{11}$	Pa-231	231 1	$4\ 72 \times 10^{10}$
C-14	14 0	$4\ 45 \times 10^{12}$	Pb 210	210 0	$7\ 63 \times 10^{13}$
Ca-41	41 0	$8\ 47 \times 10^{10}$	Pu-238	238 1	$1\ 71 \times 10^{13}$
Ce-144	144 0	$3\ 19 \times 10^{15}$	Pu 239	239 1	$6\ 20 \times 10^{10}$
Cl-36	36 0	$3\ 30 \times 10^{10}$	Pu 240	240 1	$2\ 27 \times 10^{11}$
Cm 243	243 1	$5\ 16 \times 10^{13}$	Pu 241	241 1	$1\ 03 \times 10^{14}$
Cm 244	244 1	$8\ 09 \times 10^{13}$	Pu 242	242 1	$3\ 93 \times 10^{9}$
Co-57	56 9	$8\ 46 \times 10^{15}$	Ra 226	226 1	$9\ 88 \times 10^{11}$
Co 60	59 9	$1\ 13 \times 10^{15}$	Ra-228	228 1	$2\ 72 \times 10^{14}$
Cs 134	134 0	$1\ 29 \times 10^{15}$	Ru 106	106 0	$3\ 26 \times 10^{15}$
Cs 135	135 9	$8\ 83 \times 10^{8}$	Sb-125	125 0	$1\ 03 \times 10^{15}$
Cs 137	137 0	$8\ 65 \times 10^{13}$	Sm 151	151 0	$2\ 63 \times 10^{13}$
Eu 152	152 0	$1\ 81 \times 10^{14}$	Sr-90	89 9	$1\ 38 \times 10^{14}$
Eu 154	154 0	$2\ 73 \times 10^{14}$	Tc-99	98 9	$1\ 69 \times 10^{10}$
Eu 155	155 0	$4\ 65 \times 10^{14}$	Th 228	228 1	$8\ 19 \times 10^{14}$
Fe-55	55 0	$2\ 42 \times 10^{15}$	Th 229	229 1	$2\ 14 \times 10^{11}$
Gd 152	152 0	$2\ 18 \times 10^{1}$	Th 230	230 1	$2\ 02 \times 10^{10}$
H 3	3 0	$9\ 61 \times 10^{15}$	Th 232	232 1	$1\ 09 \times 10^{5}$
I 129	129 0	$1\ 73 \times 10^{8}$	U 232	232 1	$2\ 14 \times 10^{13}$
K 40	40 0	$6\ 99 \times 10^{6}$	U 233	233 1	$9\ 63 \times 10^{11}$
Mn 54	54 0	$7\ 74 \times 10^{15}$	U 234	234 1	$6\ 23 \times 10^{9}$
Na 22	22 0	$6\ 24 \times 10^{15}$	U 235	235 1	$2\ 16 \times 10^{6}$
Nb 94	93 9	$1\ 90 \times 10^{11}$	U 236	236 1	$6\ 46 \times 10^{8}$
Ni 59	59 0	$8\ 08 \times 10^{10}$	U 238	238 1	$3\ 36 \times 10^{5}$

J.5.1 Americium

Scant information is available on the possible solid phases of americium in soil and rock environments (Ames and Rai 1978). The relative solubility of several americium solids in an oxidizing environment (pO_2 = 0 68 atm) have been estimated by Latimer (1952) and Keller (1971) as a function of solution pH On the basis of this information, the stability diagram for americium solids has been constructed by Ames and Rai (1978) as shown in Figure J 1. It can be seen that the solubility of the americium solids decreases rapidly as the solution pH increases Except for $Am(OH)_3$, changing the soil solution system from oxidized to reduced conditions will increase the activities of Am^{+3} associated with each possible solid phase

J.5.2 Antimony

Thermodynamic data for Sb_2O_3 (Sillen and Martell 1964), Sb_4O_6, $Sb(OH)_3$, Sb_2O_4, Sb_2O_5, Sb_2S_3, $SbCl_3$, and SbF_3 (Wagman et al , 1968) compounds were selected by Ames and Rai (1978) to construct the stability diagram shown in Figure J 2 for antimony solids in an oxidizing soil environment with pO_2 = 0.68 atm The $SbCl_3$, SbF_3, and Sb_2S_3 solids are very soluble in the oxidizing environment and therefore are not shown in this figure

J.5.3 Cerium

The stability diagram for cerium solids is shown in Figure J 3 The thermodynamic data for the compounds used for developing this figure were obtained from Schumm et al (1973) for Ce_2O_3 and CeO_2, Baes and Mesmer (1976) for $Ce(OH)$, and Sillen and Martell (1964) for $CePO_4$

J.5.4 Cesium

Thermodynamic data are available for the following cesium solids Cs(OH), Cs_2O, CsCl, $CsClO_4$, Cs_2SO_4, Cs_2CO_3, $CsHCO_3$, $CsNO_3$, and CsF As reported by Ames and Rai (1978), all these solids are highly soluble and, therefore, stability diagrams for cesium are not presented
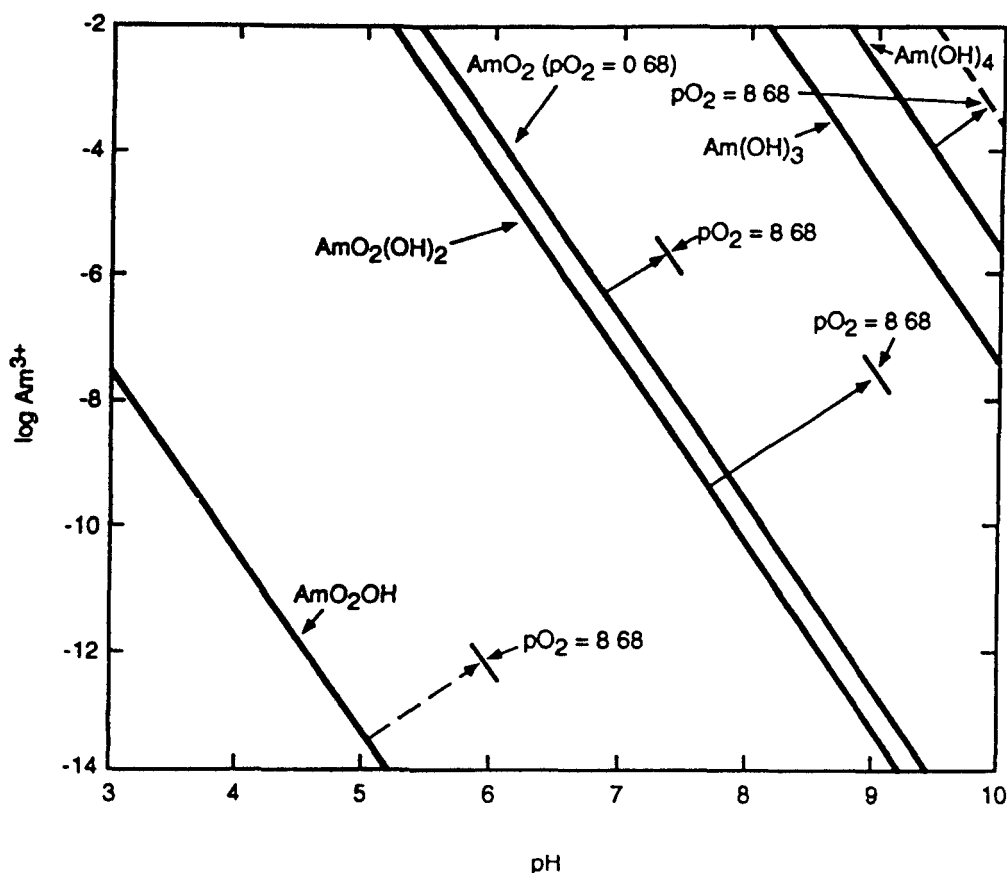
FIGURE J.1 Relative Stability of Various Americium Solids in an Oxidizing Soil Environment [$pO_{2(g)}$ = 0.68 atm] (Source: Adapted from Ames and Rai 1978)

J.5.5 Cobalt

The stability of cobalt solids depends on the pH and the oxidation-reduction environment. Sources from which thermodynamic data for various cobalt solids were obtained were Sillen and Martell (1964) for $Co(OH)_3$, $CoCO_3$, and $CoOOH$, Wagman et al (1969) for CoO and $CoHPO_4$, Robie and Waldbaum (1968) for $Co_3(PO_4)_2$, and Chase et al (1975) for Co_3O_4. The stability diagram for cobalt is shown in Figure J 4

J.5.6 Curium

Curium can form hydrides, hydroxides, halides, oxides, and organometallic compounds (Keller 1971) A search for thermodynamic data for these compounds was
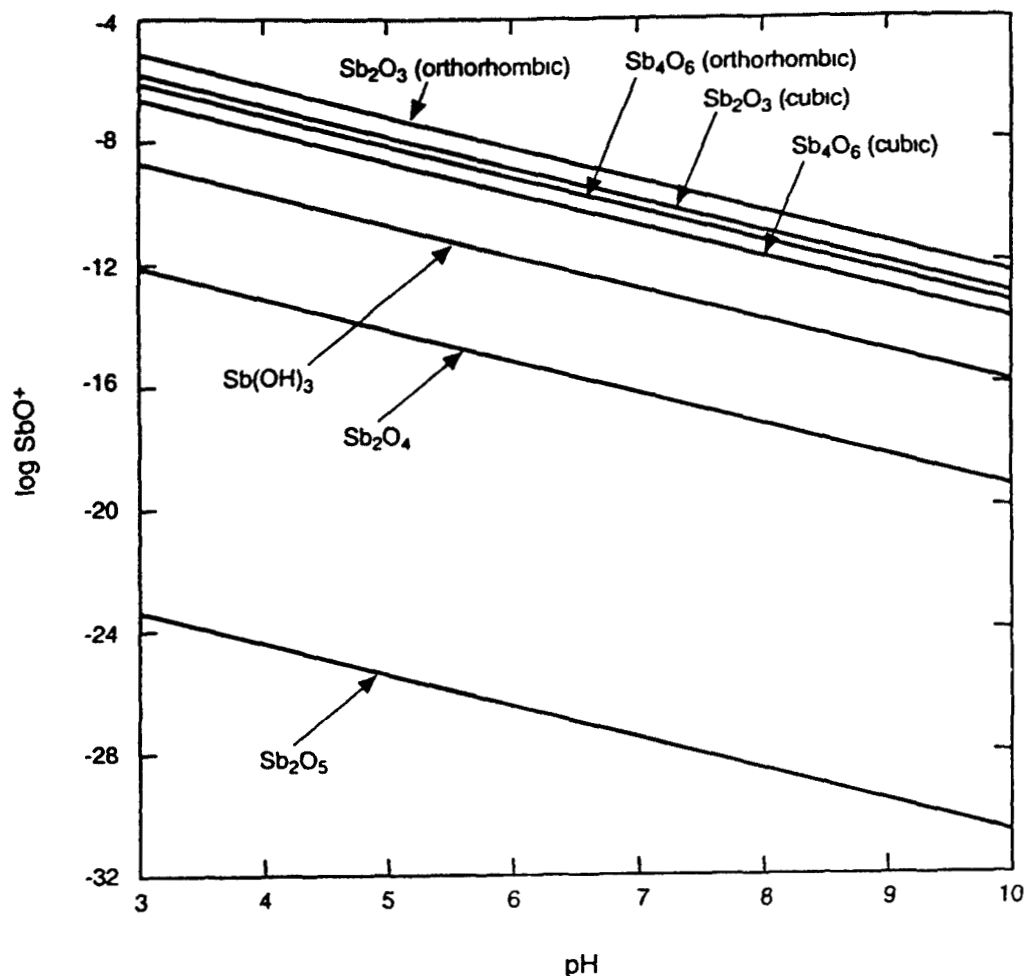
FIGURE J.2 Activity of SbO⁺ in Equilibrium with Various Antimony Solids in an Oxidizing Soil Environment [$pO_{2(g)}$ = 0 68 atm] (Source: Adapted from Ames and Rai 1978)

unsuccessful except for CmF_3 Therefore, a stability diagram for curium cannot be developed at this time

J.5.7 Europium

Europium forms oxides, hydroxides, and salts with chlorides and sulfates The stability diagram for europium is shown in Figure J 5 The thermodynamic data for the compounds used for developing this figure were obtained from Shumm et al (1973) for Eu_2O_3 and $Eu(OH)_3$ and Latimer (1952) for $Eu_2(SO_4)_3$ $8H_2O$ The other solids were too soluble and fall beyond the graph boundaries

50
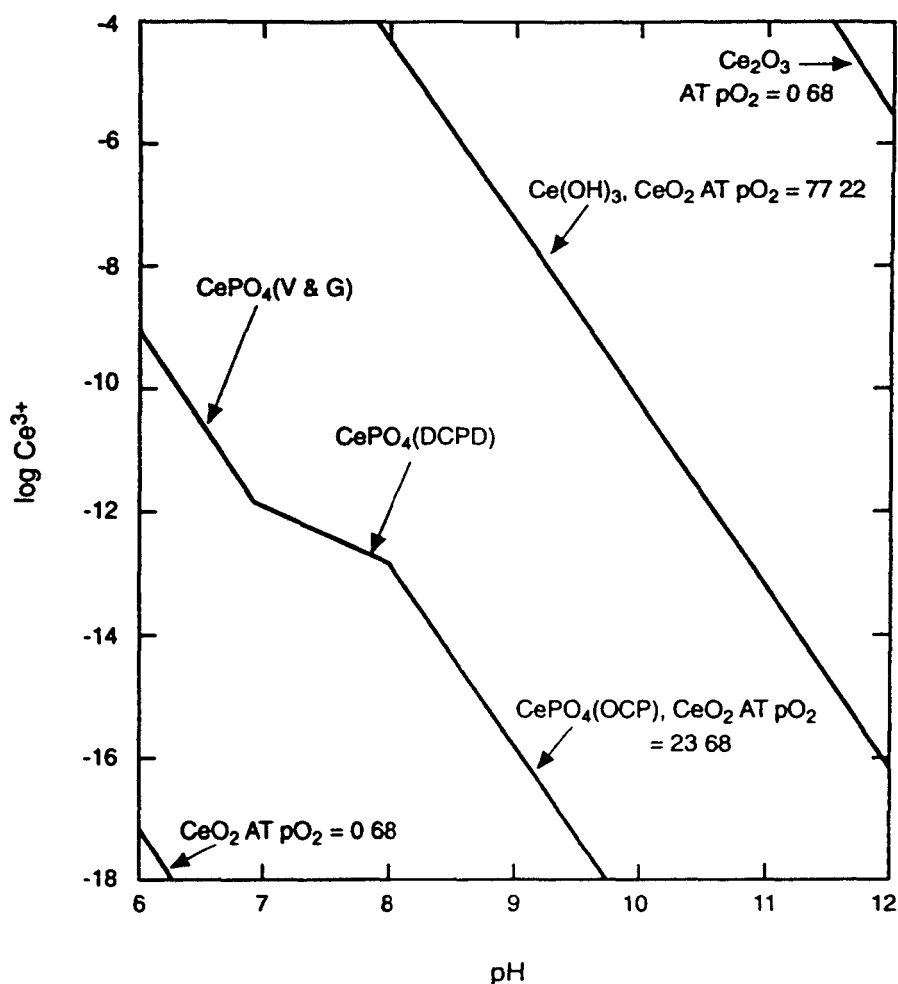
FIGURE J.3 Activity of Ce^{3+} in Equilibrium with Phosphate Levels from Variscite and Gibbsite (V & G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP) (Source: Adapted from Ames and Rai 1978)

J.5.8 Iodine

Most iodine compounds are very soluble Some of the insoluble or sparingly soluble compounds include the iodites of lead and palladium, the hypoiodites of silver and mercury, and barium periodates (Pourbaix 1966) In normal soils, the concentration of most of these elements (lead, palladium, arsenic, mercury, and barium) that form compounds with iodine is very low (Ames and Rai 1978) Therefore, they would not be present in soils
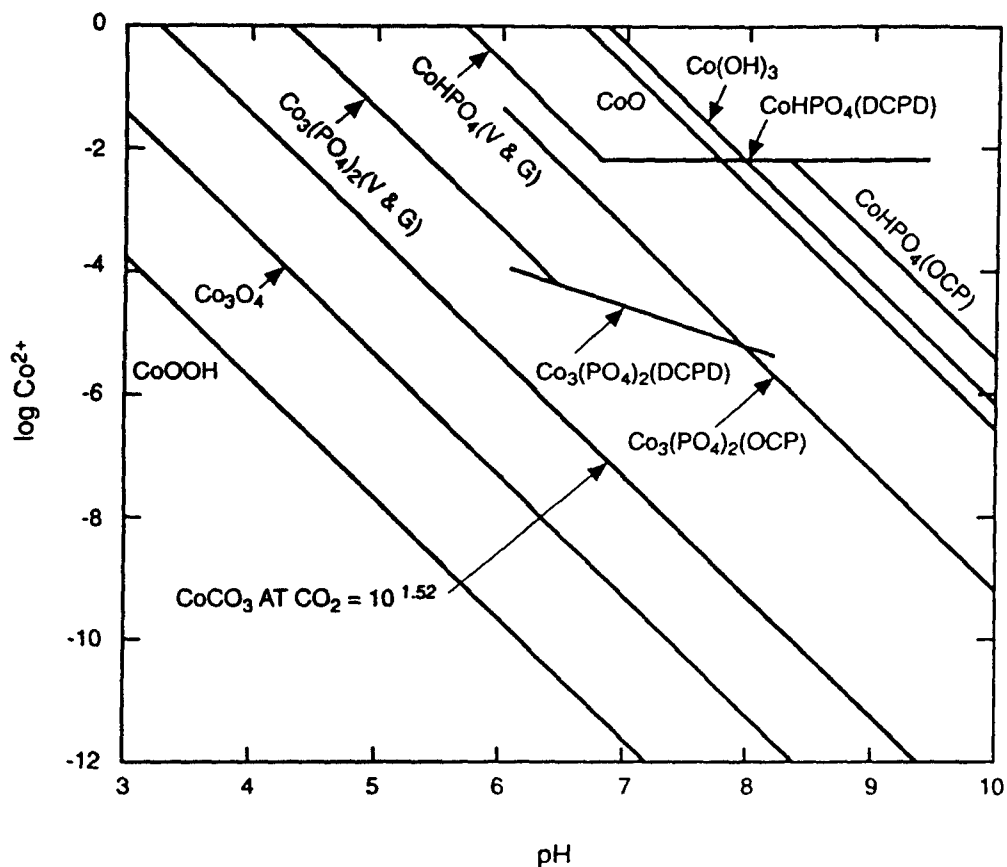
FIGURE J.4 Relative Stability of Cobalt Solids in an Oxidizing Soil Environment [pO$_{2(g)}$ = 0.68 atm, pCa^{2+} = 2.5] with Phosphate Levels in Equilibrium with Variscite and Gibbsite (V & G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP) (Source: Adapted from Ames and Rai 1978)

J.5.9 Neptunium

Thermodynamic data are unavailable for neptunium compounds other than oxides and hydroxides (Burney and Hartour 1974) The stability diagram for neptunium shown in Figure J 6 relates the activity of NpO$_2^+$ to pH in an oxidizing environment (pO$_2$ = 0 68 atm) in equilibrium with neptunium oxides and hydroxides

J.5.10 Plutonium

The stability diagram for plutonium shown in Figure J 7 relates the activity of Pu^{+4} to pH in an oxidizing environment (pO$_2$ = 0 68 atm) in equilibrium with various plutonium solids The parameters indicated in parentheses after the mineral formulas refer to the
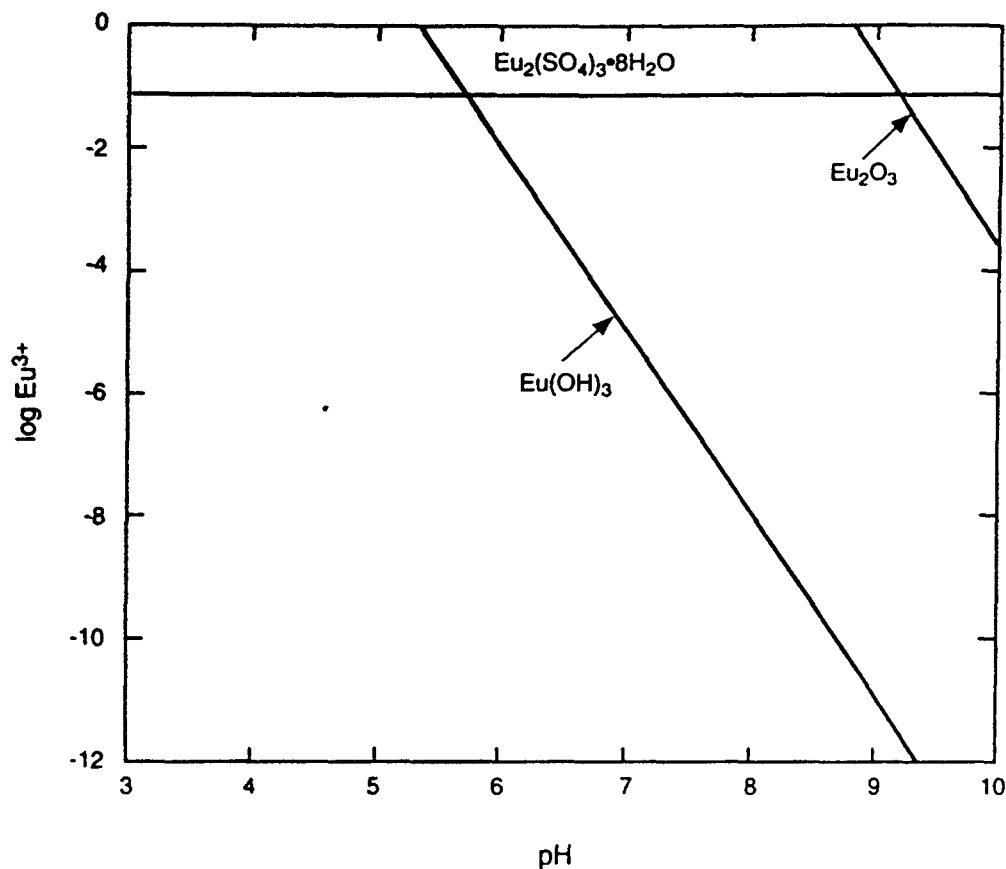
**FIGURE J.5 Relative Stability of Various Europium Solids at
pSO_4^{2-} = 2.5 (Source: Adapted from Ames and Rai 1978)**

additional condition of equilibrium   For example, (V&G) indicated after the $Pu(HPO_4)_2$
mineral formula denotes that the mineral is considered to be in equilibrium with variscite
and gibbsite

J.5.11 Radium

The compounds formed by radium and their solubilities are similar to barium
Thermodynamic data for radium compounds are available only for radium nitrate, chloride,
iodate, and sulfate (Parker et al 1971) All of the compounds except radium sulfate are very
soluble   Therefore, the stability diagram for radium compounds is not presented   The
solubility product for radium sulfate is 4 25 × 10^{-11} at 25°C and 1 atm
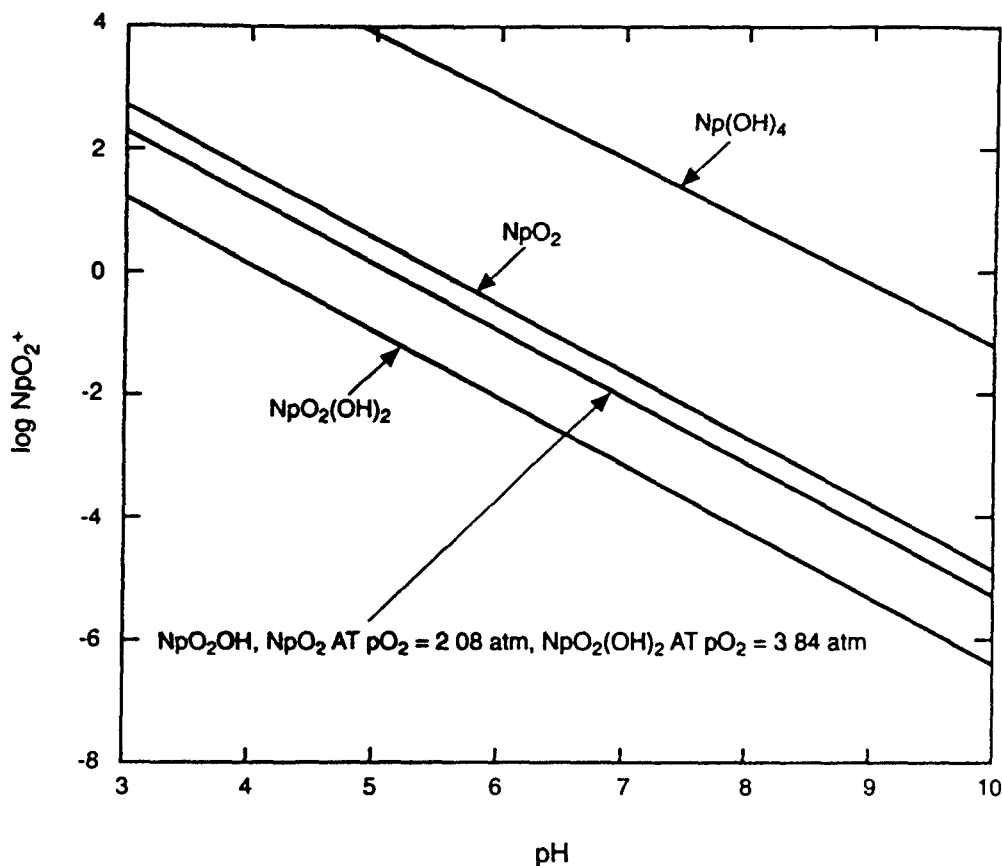
FIGURE J.6 Relative Stability of Various Neptunium Solids in an Oxidizing Soil Environment [$pO_{2(g)}$ = 0.68 atm] (Source: Adapted from Ames and Rai 1978)

J.5.12 Ruthenium

Ruthenium is generally present in association with platinum group metals Ruthenium can also form discrete solid compounds such as RuO_2, RuO_4, $Ru(OH)$, $Ru(OH)_4$, $RuCl_3$, and RuS_2 The stability diagram for ruthenium solids under oxidizing conditions (pO_2 = 0 68 atm) is shown in Figure J 8 The thermodynamic data for $Ru(OH)_3$ and $Ru(OH)_4$ were obtained from Sillen and Martell (1964), the data for RuO_2 and RuO_4 were obtained from Wagman (1969)

J.5.13 Strontium

Strontium is an alkaline-earth and forms several salts Thermodynamic data for various strontium compounds are available in the literature Except for $SrSiO_3$, $SrHPO_4$,
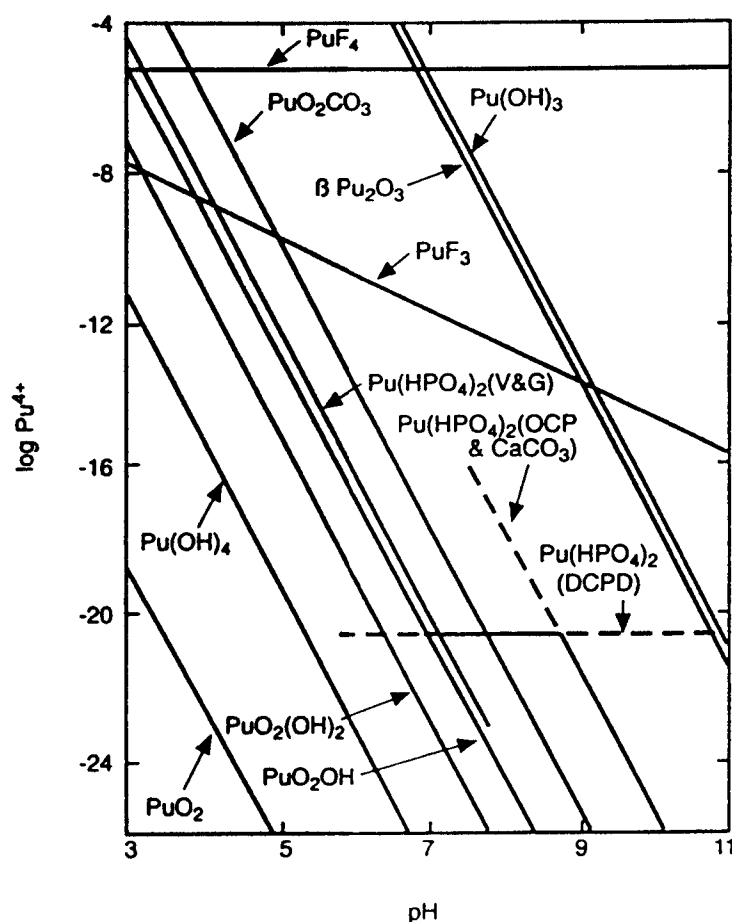
FIGURE J.7 Relative Stability of Various Plutonium Solids in an Oxidizing Soil Environment [pO$_{2(g)}$ = 0.68 atm, pCO$_{2(g)}$ = 3.52 atm], pF⁻ = 3.5, with Phosphate Levels in Equilibrium with Variscite and Gibbsite (V & G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP) (Source: Adapted from Ames and Rai 1978)

Sr$_3$(PO$_4$)$_2$, SrCO$_3$, and SrSO$_4$, the strontium solids are too soluble to construct a stability diagram. As shown in Figure J 9, the stability diagram for strontium was developed on the basis of thermodynamic data from Sillen and Martell (1964) for Sr$_3$(PO$_4$)$_2$ and Parker et al (1971) for SrSiO$_3$, SrHPO$_4$, SrCO$_3$, and SrSO$_4$
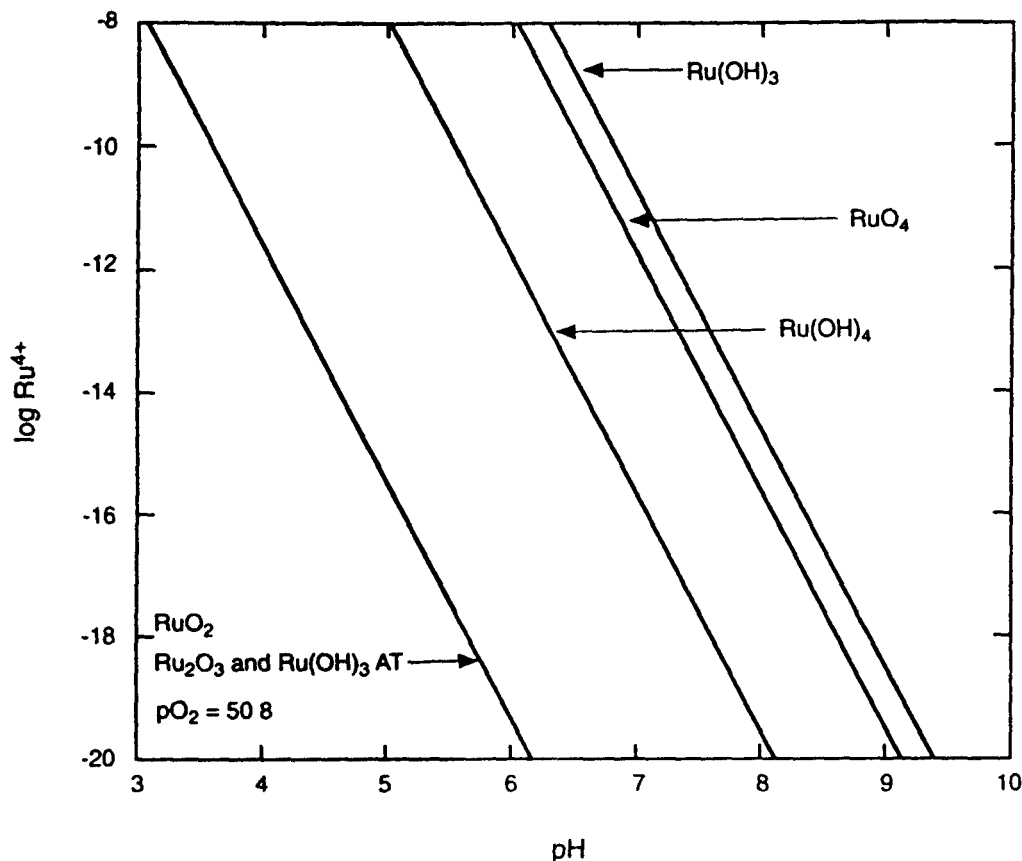
FIGURE J.8 Relative Stability of Various Ruthenium Solids in an
Oxidizing Soil Environment [$pO_{2(g)}$ = 0.68 atm, pCl^- = pSO_4^{2-} = 2.5]
(Source. Adapted from Ames and Rai 1978)

J.5.14 Technetium

Baes and Mesmer (1976) reported that technetium (VII) forms strong peracids (HMO_4) and that its oxides are very soluble Scant information is available concerning the solubility of its salts (Ames and Rai 1978)

J.5.15 Thorium

Common insoluble thorium compounds include hydroxides, fluorides, and phosphates Soluble compounds include chlorides, nitrates, and sulfates The stability diagram for thorium, as shown in Figure J 10, is constructed for an assumed environmental condition of equilibrium with various thorium solid phases The thermodynamic data for $ThO_2(s)$ were selected from Baes and Mesmer (1976) The data for the other compounds were selected from Sillen and Martell (1964)
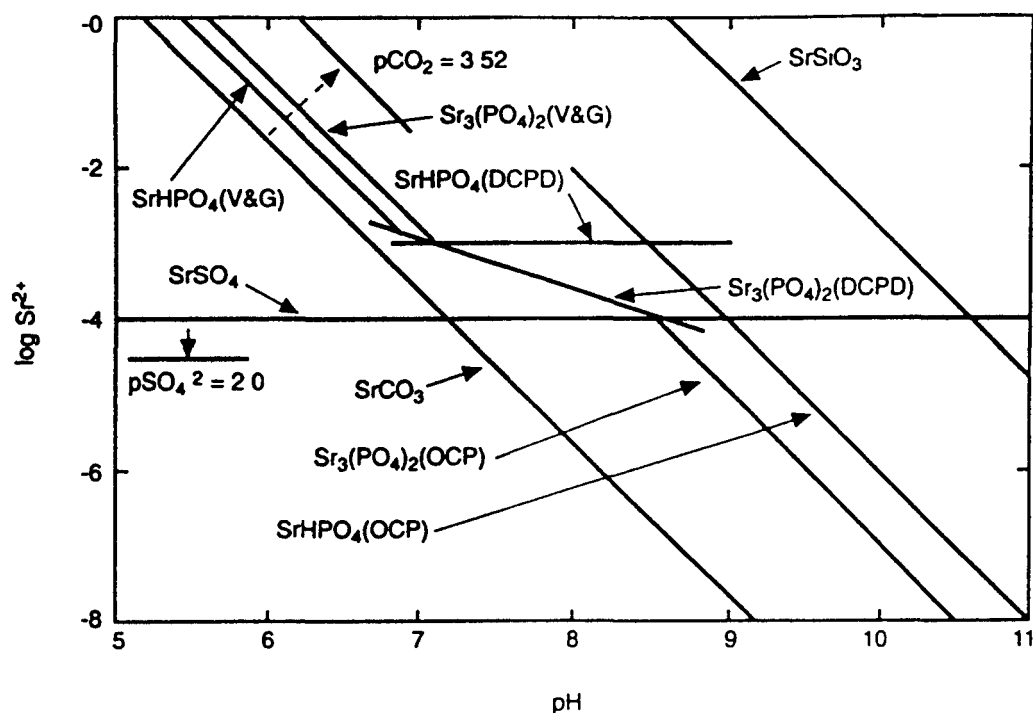
56

FIGURE J.9 **Relative Stability of Various Strontium Solids at pCa^{2+} = pSO$_4$$^{2-}$ = 2.5, pH$_4$SiO$_4$ = 3.1, and pCO$_{2(g)}$ = 1.52 atm in Equilibrium with Variscite and Gibbsite (V & G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP) (Redox potential has little effect on strontium solubilization.) (Source: Adapted from Ames and Rai 1978)**

J.5.16 Tritium

Tritium is a radioactive isotope of hydrogen Thus, the behavior of tritium in soils would be expected either to be similar to hydrogen or to exist as an ion, gas, or liquid (tritiated water) In the soil solution system investigated, tritium can travel rapidly at about the same velocity as the soil water or groundwater

J.5.17 Uranium

The stability diagram of uranium solids presented by Ames and Rai (1978) in terms of the uranyl ion activity is shown in Figure J 11 Thermodynamic data for (1) Na$_2$UO$_4$ and UO$_2$CO$_3$ were obtained from Garrels and Christ (1965), (2) data for UO$_2$(OH)$_2$, UO$_2$(OH)$_2$ H$_2$O, and Na$_4$UO$_2$(CO$_3$)$_3$ were obtained from Sillen and Martell (1964), and (3) the remaining species were obtained from Palei (1963)
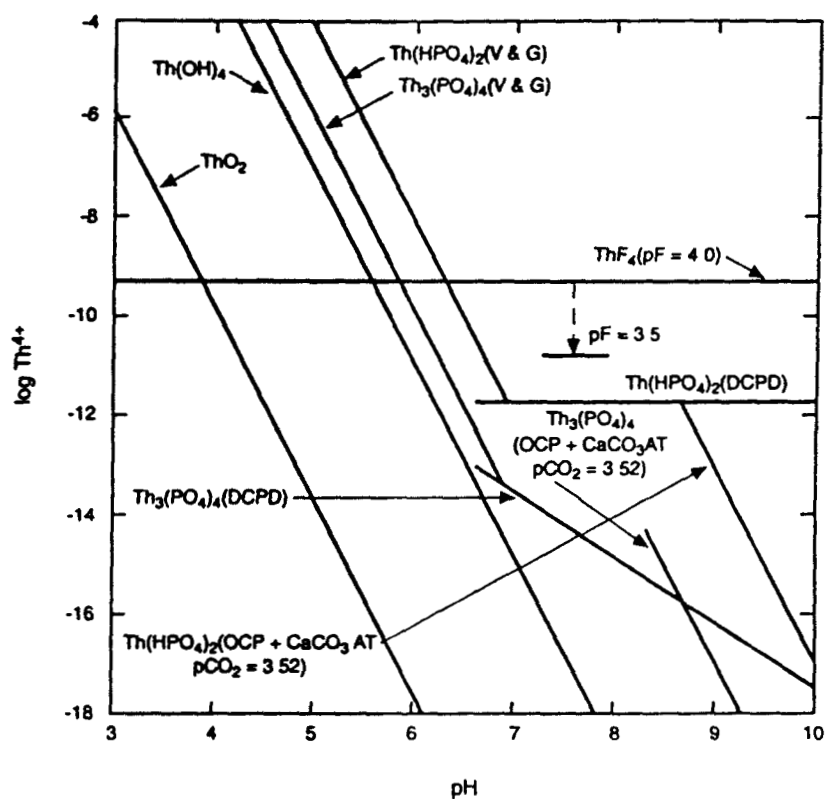
FIGURE J.10 Relative Stability of Various Thorium Solids in Equilibrium with Variscite and Gibbsite (V & G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP) (Source: Adapted from Ames and Rai 1978)
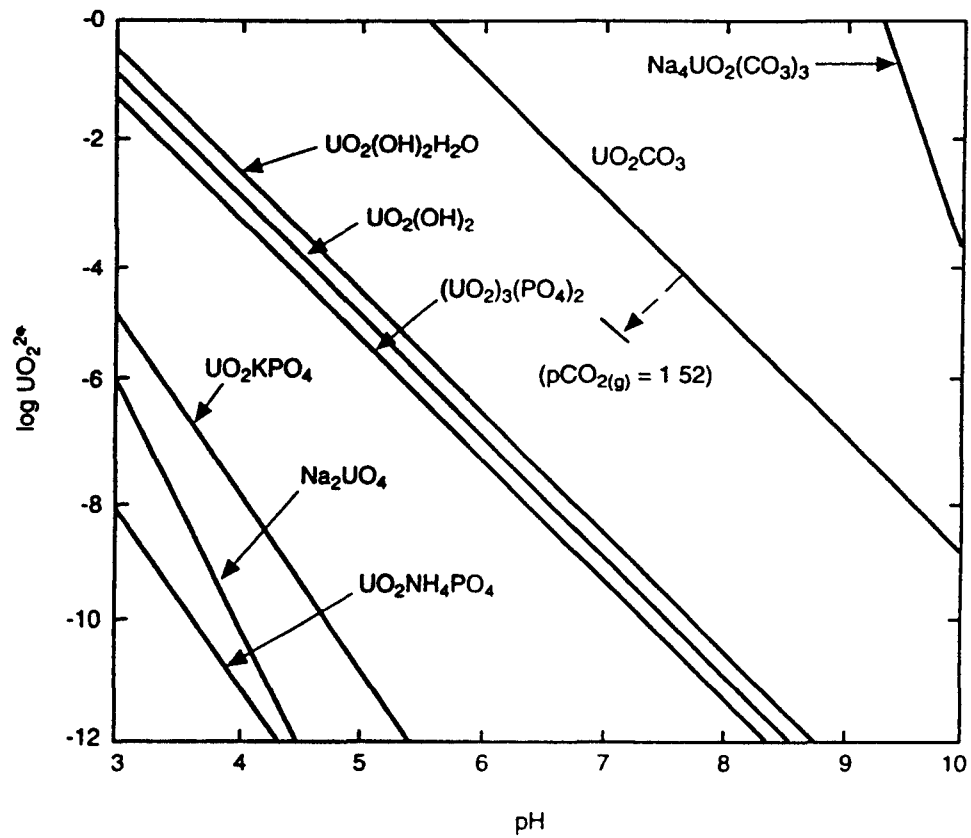
58

FIGURE J.11 Relative Stability of Various Uranium Solids in an Oxidizing Soil Environment [$pO_{2(g)}$ = 0.68 atm, $PCO_{2(g)}$ = 3.52, and pNa^+ = pNH_4^+ = 3.0] with Phosphate Levels in Equilibrium with Variscite and Gibbsite (V & G) (Source: Adapted from Ames and Rai 1978)

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